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THE STRUCTURE AND OPTICAL BEHAVIOUR OF CHALCEDONY

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(Communicated by Prof. Sir C. V. Raman, F.R.S., N.L.)

1. Introduction

Chalcedony is a cryptocrystalline variety of silica occurring in a massive form and exhibiting a waxy lustre. It is only slightly inferior to quartz in hardness and has a density lying between 2·60 to 2·64. A small percentage of water may often be found in the material. The refractive index averages at 1·537 and is thus not very different from that of quartz. Thin sections exhibit a fibrous character under the microscope and the material shows a distinct birefringence which is of the same order of magnitude as that of quartz.

Mineralogists formerly regarded chalcedony as a distinct crystalline species of silica and classed it under the orthorhombic system. But the X-ray pattern of powdered chalcedony is identical with that of quartz, as was first reported by Washburne and Navias[1] and later confirmed by Rinne,[2] thus demonstrating that chalcedony is composed of crystallites of quartz. The fibrous character of the material and the birefringence exhibited by it indicate that the crystallites have preferred orientations. Correns and Nagelschmidt[3] showed that such orientation is actually observable in the X-ray patterns of unpowdered chalcedony. The crystallites were found to be orientated around the $[1\bar{1}00]$ direction in a specimen from Olomuczan and around the $[11\bar{2}0]$ direction in a specimen from Iceland. More recently, Novak[4] has reported that the fibres of chalcedony are usually elongated along the *c*-axis or the *a*-axis of quartz.

In a recent paper[5] by Sir C. V. Raman and the present writer in these *Proceedings*, investigations on the origin of the iridescence exhibited by certain varieties of agate have been reported. By detailed optical and X-ray studies it was shown that the banded structure in iridescent agate responsible for the diffraction effects is a result of the orientation of the quartz crystallites with their *a*-axes common and the *c*-axes lying in the plane of banding in a periodic manner. It was thought worthwhile, in this connection, to

apply similar optical and X-ray methods to the case of common chalcedony. The results are presented in the following pages.

2. SOME THEORETICAL CONSIDERATIONS

Before proceeding to describe the results of the present investigation, it is useful to set out here some considerations of a general character regarding the optical behaviour of a medium consisting of crystallites of birefringent material. As is well known, quartz is a uniaxial positive crystal, the optic axis being coincident with its c-axis. The two refractive indices for the sodium light are respectively $n_e = 1{\cdot}553$ and $n_o = 1{\cdot}544$. Though this birefringence is small, it is nevertheless large enough to profoundly influence the propagation of light through the medium, as we shall proceed to show.

We shall consider first the case of a completely random orientation of the crystallites. This situation would result in a beam of light entering the material being rapidly extinguished by the process of diffusion in its passage, unless the crystallites are exceedingly small or the total optical path very short. This can be demonstrated by the following argument. Consider a plane-polarised beam of light incident on a thin lamina of the material. For simplicity, we shall assume the crystallites to lie with their c-axis parallel to the vibration of the incident light over some parts of the area of the lamina, while in the other parts they lie with their a-axis parallel to the vibration direction. The light wave passing through the two different sets of areas will travel with different velocities, thus giving rise to differences in phase. As in the theory of the Christiansen experiment discussed in these *Proceedings* by Sir C. V. Raman,[6] these differences in phase and the interferences resulting therefrom would cause a diminution in the intensity of the transmitted light. When numerous such laminæ are present following each other, the process is repeated, and if the total optical path is sufficiently large, the whole of the incident light would be diffused in its passage through the medium.

We may go a little further and describe the position in a semi-quantitative fashion by taking over the formula derived in the theory of the Christiansen experiment for the transmitted radiation, namely $I = I_0 \cdot e^{-\pi^2 (\mu_1 - \mu_2)^2 \cdot \Delta^2 \cdot z / \lambda^2}$. Here μ_1 and μ_2 are respectively the maximum and the minimum refractive indices of quartz for the wavelength λ, Δ is the size of the individual crystallite, and z is the total optical path traversed. The influence of these variables Δ, z and λ on the transmission may be illustrated by a few calculations made on the basis of the above formula. Thus for example, taking $\Delta = 1\,\mu$, $z = 1$ mm. and $\lambda = 0{\cdot}7\,\mu$ or $0{\cdot}4\,\mu$, the transmission is 18% and 1% respectively for the two wavelengths. Thus there would be a marked reddening of the light as it penetrates through the

material. The influence of the size of the crystallites is shown by the following calculation. When $z = 1$ mm., $\lambda = 0{\cdot}5\,\mu$ and $\Delta = \frac{1}{2}\,\mu$ or $2\,\mu$, the transmission is 20% and 0·2% respectively showing that it falls off very rapidly with increasing size of crystallites. Increasing the length of the optical path from $z = 1$ mm. to $z = 2$ mms., for $\Delta = \frac{1}{2}\,\mu$, and $\lambda = 0{\cdot}5\,\mu$ similarly results in a marked decrease of transmission from 20% to 4%. It should be remarked that the light which disappears from the incident beam would appear as diffused or diffracted radiation in various directions sorrounding the direction of the incident beam. From the arguments stated, it is clear that with incident unpolarised light, the transmitted light, if any, would also be unpolarised, and so also the diffused radiation.

The situation is totally different when we consider the case where the crystallites are all orientated with their *c*-axes as a common direction but, with their *a*-axes lying in a random manner in a perpendicular plane. The uniaxial character of quartz would result in the material exhibiting perfect transparency, irrespective of whether the direction of propagation is along the orientation axis or in the perpendicular direction, since the randomness in the positions of the *a*-axes leaves the principal optical vibration directions unaltered. The material would, in fact, be optically equivalent to a single crystal of quartz.

Another type of ordering of the crystallites requiring consideration is the *a*-axis orientation. Here the crystallites may be thought of as forming elongated fibres with their *a*-axes lying parallel to the length of the same but with their *c*-axes differently orientated. Consider a plate which is made up of a bundle of such fibres running parallel to each other and also to the surface of the plate. The fact that all the crystallites of quartz are orientated with their *a*-axes common would fix the positions of the fast optic vibration direction, which would be identical for all the crystallites, and as such the material would behave as an optically homogeneous medium for a light wave vibrating along the length of the fibres. Consequently, a plane polarised light wave incident normally on the plate of the material with its vibration direction parallel to the length of the fibres would be freely transmitted. On the other hand, if the light vibrates transversely to the length of the fibres, it would be strongly diffused. This follows from a consideration of the fact that the orientation of the *c*-axis alters as the light wave advances from one crystallite to the other, thus giving rise to fluctuations in the refractive indices. The size of the individual crystallites and the thickness of the plate would influence its behaviour for this direction of incident vibration in the same manner as that considered earlier for the case of random orientation. Hence, if unpolarised light is incident normally on the plate and if the same

is sufficiently thick, the light transmitted would be completely polarised with its vibration parallel to the length of the fibres, while the light diffused would appear as a brush of light drawn out in directions transverse to the fibre length, and would be polarised with its vibration normal to the fibre length. The transmitted light would however exhibit partial polarisation if the plate is thin, since the component vibrating transversely to the fibres would also then be transmitted to some extent.

We now proceed to consider the optical behaviour of a plate of the material which is assumed to have a laminated structure, the planes of lamination being perpendicular to the surface of the plate. The crystallites of quartz composing the material are further assumed to be orientated with their *a*-axes parallel to the common normal to the laminæ, while the *c*-axes in each individual lamina has everywhere the same orientation, this however being different for the different laminæ. If plane-polarised light wave is incident on the plate normally, the optical behaviour exhibited by it would depend on whether the vibration direction of the incident wave coincides with the common direction of the *a*-axis or is perpendicular to it. In the former case, it is at once evident that the material would behave as if it were optically homogeneous and the emergent light wave would have the same phase retardation over the entire area of the plate. If on the other hand, the incident light vibrates perpendicular to the common direction of the *a*-axis, it would be freely transmitted by each lamina, because of the identical orientations of the *c*-axes of the crystallites in it; but the light emerging from the different laminæ would be retarded to different extents, in view of the fact that the orientation of the *c*-axis varies from lamina to lamina. Thus, differences in phase would be introduced and these would be of the order of several wavelengths even for plates only a fraction of a millimetre in thickness. In consequence, the light would be diffracted away in various directions lying in a plane perpendicular to the laminæ. In the particular case where the orientations of the *c*-axes in the laminæ are repeated at regular intervals, the plate would function as a phase-change diffraction grating giving several orders of spectra. The laminated structure would accordingly be visible if the plate be viewed with incident polarised light vibrating in the plane of the laminæ, but would disappear when viewed with light vibrating in a perpendicular direction.

3. TRANSMISSION AND DIFFUSION OF LIGHT

The theoretical considerations set forth in the preceding section clearly indicate that the optical behaviour of a medium consisting of crystallites of quartz would be very much influenced by its thickness. Accordingly, five

plates of different thicknesses ranging from 2 mms., down to about 0·15 mm. were cut and polished out of translucent and colourless agate or chalcedony, specimens of which were available in the Museum of the Institute. We now proceed to describe and illustrate the various optical effects exhibited by a typical specimen.

The particular plate was sliced out of a lump of colourless, translucent agate, and measured 2 cms. in length, 1·5 cm. in width, and 1 mm. in thickness. When viewed directly against a lighted window, it exhibits a characteristic structure, the transparency of the plate varying enormously over its area. Certain regions appear bright while others are seen as dark cloudy patches. The situation however is completely different when the specimen is viewed against a dark background with the light falling on it rather obliquely; the dark portions now appear bright and *vice versa*. This is illustrated in the photographs reproduced as Figs. 1 and 2 in Plate XXXIII taken respectively by direct and by diffracted light. Their complementarity is particularly evident on a comparison of the areas depicted on the right of Figs. 1 and 2; the dark patches in the one appear as bright patches in the other. The region to the extreme left in Fig. 1 which is seen in the photograph as a dark area is actually very bright when the plate is viewed directly against an extended source of light.

The optical behaviour of the different parts of the specimen is better appreciated when a narrow bright source of light is viewed through the plate with the latter held close to the eye of the observer. When thus examined, the light source itself cannot be seen through the areas depicted on the right-hand side of Fig. 2; only an extended patch of diffuse light is observed. On the other hand, the light source is seen well defined, though somewhat diminished in intensity, if the plate is viewed through the area appearing dark towards the left of Fig. 2. The light source, however, appears overlaid by a narrow brush of diffused light, which extends on either side of it through a considerable range of angles. A remarkable feature of the light regularly transmitted by the plate is that it is fully polarised and therefore totally extinguished by a polaroid appropriately orientated and placed in the path of the light. When the vibration direction of the polaroid is parallel to the brush of diffuse light, the transmitted light is cut off. The diffused light also exhibits a high degree of polarisation, its intensity being a minimum when the vibration direction of the polaroid is perpendicular to the extension of the brush, thus indicating that the latter is polarised in the opposite sense to the transmitted light.

The observations described above are illustrated in Figs. 6 and 7 of Plate XXXIV. Fig. 6 was recorded with the specimen mounted inside a

camera, the latter focussing a brightly illuminated circular aperture placed at a distance from the camera lens. The plate was kept 4 cms. away from the photographic film and the entire beam passed through the region of the specimen already referred to. It will be noticed on an inspection of Fig. 6 that the light transmitted appears as a well-focussed central image, overlaid by a diffuse brush of light. The photograph reproduced as Fig. 7 was recorded with the same arrangements but with a double-image prism of quartz placed in front of the camera lens. As a result of this combination, the incident beam of light is split into two polarised components vibrating in perpendicular directions. The plate was suitably orientated so as to exhibit the polarisation of the transmitted light and the diffuse brush most clearly. The two images appearing in Fig. 7 represent respectively the components vibrating perpendicular and parallel to the diffuse brush. It will be noticed that the image of the light source is clearly seen in the former and is invisible in the latter. *Per contra*, the diffuse brush is more intense in the latter than in the former. These observations described are in full agreement with the behaviour envisaged in Section 2 above for a medium consisting of crystallites of quartz orientated with their *a*-axes common. It may therefore be inferred that the material has a fibrous structure and that the crystallites of quartz are orientated with their *a*-axes along the length of the fibres.

4. SOME FURTHER OBSERVATIONS

Thus, as we have seen, theoretical considerations and actual observations alike demonstrate that the manner in which the crystallites of quartz are orientated in it profoundly influence the optical behaviour of chalcedony. Another factor which has to be considered and indeed is scarcely less important is the length of the optical path, in other words the thickness of the plate. A study of the behaviour of plates both thinner and thicker than that dealt with in the preceding section shows this very clearly.

As an example, we may refer to the case of a plate 0·15 mm. thick which was examined. It exhibited a notable measure of transparency over its entire area, though from the manner in which the light was diffused in passage through the plate, it was quite clear that the crystallites in it did not possess any specificity of orientation. Neither the transmitted light nor the diffused radiation exhibited any observable measure of polarisation. Examination of the piece on the stage of a polarising microscope between crossed nicols confirmed these inferences. In a number of places a radiating fibrous structure was seen exhibiting a dark cross. An example of this is illustrated in the microphotograph reproduced as Fig. 10 in Plate XXXV.

Another plate 0·3 mm. thick the optical behaviour of which was studied gave some interesting results. In many respects it resembled the 1 mm. thick plate considered in Section 3, but it was distinctly more transparent over its whole area. Nevertheless large local variations in transparency were observable. In the regions where the image of the source was seen most brightly the latter appeared overlaid by an elongated brush of diffused light. The polarisation of the transmitted light was *less* perfect, and the polarisation in the opposite sense of the brush of diffuse light *more* perfect than in the case of the 1 mm. thick plate. These features which are in agreement with the indications of theory will be evident from the photograph taken with a double image prism and reproduced as Fig. 8 of Plate XXXIV.

The decreasing transparency resulting from the increase in length of the optical path is further illustrated by observations made with a plate of 2 mms. thickness. Even in its most transparent regions, the source of light seen through it was much less intense than in the case of the 1 mm. thick plate and also showed a distinct reddish tinge. The polarisation of the transmitted light was however visibly perfect in such areas. *Per contra*, the polarisation of the brush of diffuse light was noticeably imperfect.

5. The Lamellar Structure; Its Nature and Optical Characters

A coarsely banded structure, often following in its course the naturally occurring external boundary of the material, is a very common feature exhibited by chalcedony. Examples of this are illustrated in Fig. 3, Plate XXXIII, the photograph being by transmitted light and in Figs. 4 and 5 of Plate XXXIII, taken respectively by transmitted and diffracted light. The photographs were recorded with specimens cut and polished normal to the planes of banding, the piece illustrated in Fig. 3 being 2 mms. thick and that illustrated in Figs. 4 and 5 being 1 mm. thick. The influence of the shape of the external surface of the material on the configuration of the banding is very conspicuous in Fig. 3. The complementarity of the appearance of the chalcedony as seen by transmitted and diffracted light is remarkably well shown by Figs. 4 and 5 in Plate XXXIII.

As will be seen from Figs. 3 and 4, the transparency of the material varies notably in the case of both the specimens, the most transparent area in each being a broad band running through the centre. When a distant bright source of light is viewed through this area, a well-defined image of the source can be seen, accompanied by a brush of diffuse light running in a direction parallel to the planes of banding. When the specimen is moved laterally, the direction of the brush follows the course of banding. From

what has already been described in the preceding section, it is clear that the planes of banding are everywhere transverse to the length of the fibres, which as already explained are themselves parallel to the *a*-axis of the crystallites. Analogous features are also visible in the more heavily banded areas in which the transmitted light is very feeble. In these latter areas the coarsely fibrous structure of the material is very obvious. This can be seen from the picture reproduced as Fig. 12 in Plate XXXV which is an enlarged photograph of an area of the specimen illustrated on a smaller scale in Fig. 4. Fig. 12 also exhibits numerous closely-spaced lamellæ which are not visible in Fig. 4. This is a general feature in the case of both specimens.

The fibrous structure of chalcedony in which the *a*-axes of the crystallites of quartz are parallel to the fibre length is often, if not invariably, accompanied by a lamellar structure with its planes running everywhere transverse to the fibres. Such a structure is most clearly seen through a magnifier when the area under observation lies on the boundary between light and darkness, when the plate is held and viewed against a source of light. It is seen very clearly in Fig. 1, Plate XXXIII in the region to the left and in the lower parts of the figure. A remarkable characteristic of this fine lamellar structure is the appearance of numerous ripples or waves running approximately parallel to it over the area of the specimen. This feature is illustrated by micro-photographs recorded under low-magnification and reproduced as Figs. 9 and 11 respectively in Plate XXXV. The photographs were taken with a polaroid interposed between the plate and the objective of the microscope, the vibration transmitted by the polaroid being parallel to the planes of banding in Fig. 9, and being transverse to it in Fig. 11. As will be seen on a comparison of the two figures, the rippling is very clearly seen in Fig. 9 and is scarcely visible in Fig. 11. It should also be mentioned in this connection, that a small distant source of light viewed through the area exhibits, superposed on the diffuse brush of light, a series of diffraction spectra on either side. Whereas the source of light itself is almost completely extinguished when a polaroid is interposed with its vibration direction parallel to the planes of banding, the diffraction spectra referred to are not extinguished and indeed are generally better seen in that position of the polaroid.

It may be mentioned here that the light transmitted is greatly influenced by the tilt of the specimen, rapidly diminishing in intensity when the plate is tilted in such manner that the planes of banding make increasing angles with the incident beam of light.

From the foregoing observations, we are entitled to infer that the lamellar structure and the fine ripples seen accompanying it are a consequence of a

FIG. 1

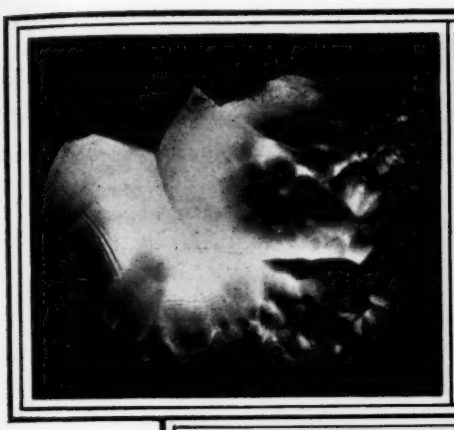


FIG. 2

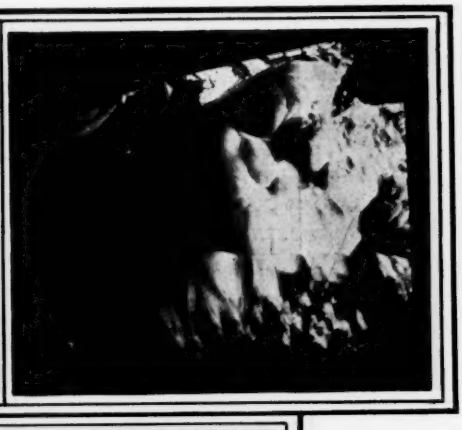
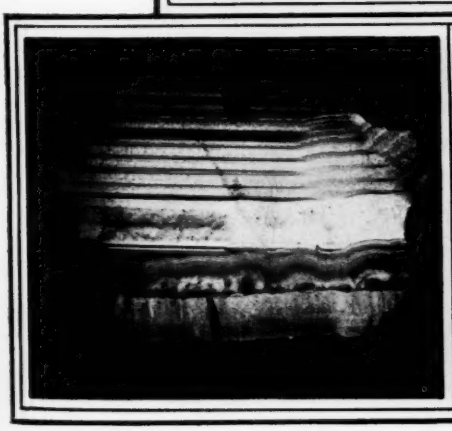


FIG. 3



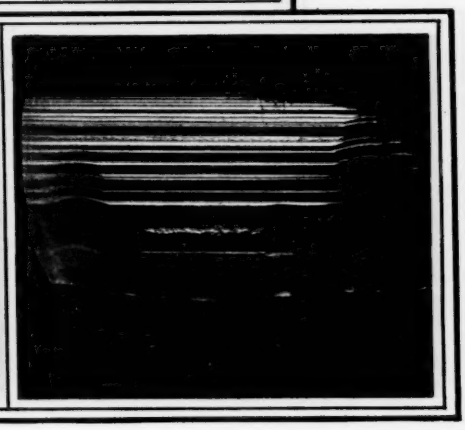


FIG. 4

FIG. 5

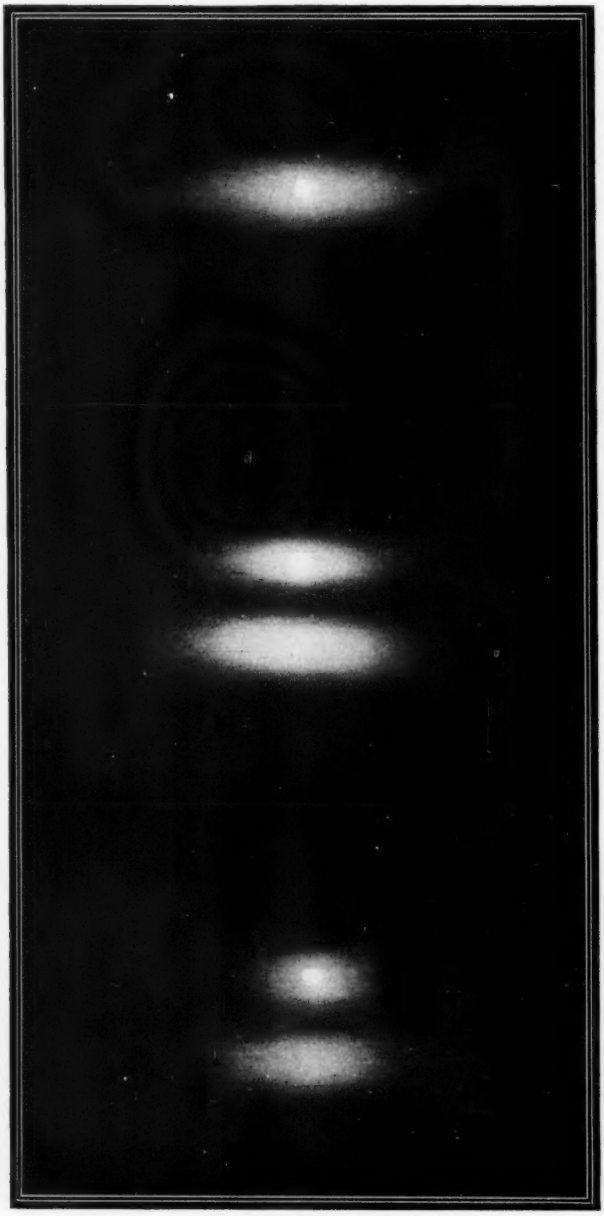


FIG. 6

FIG. 7

FIG. 8

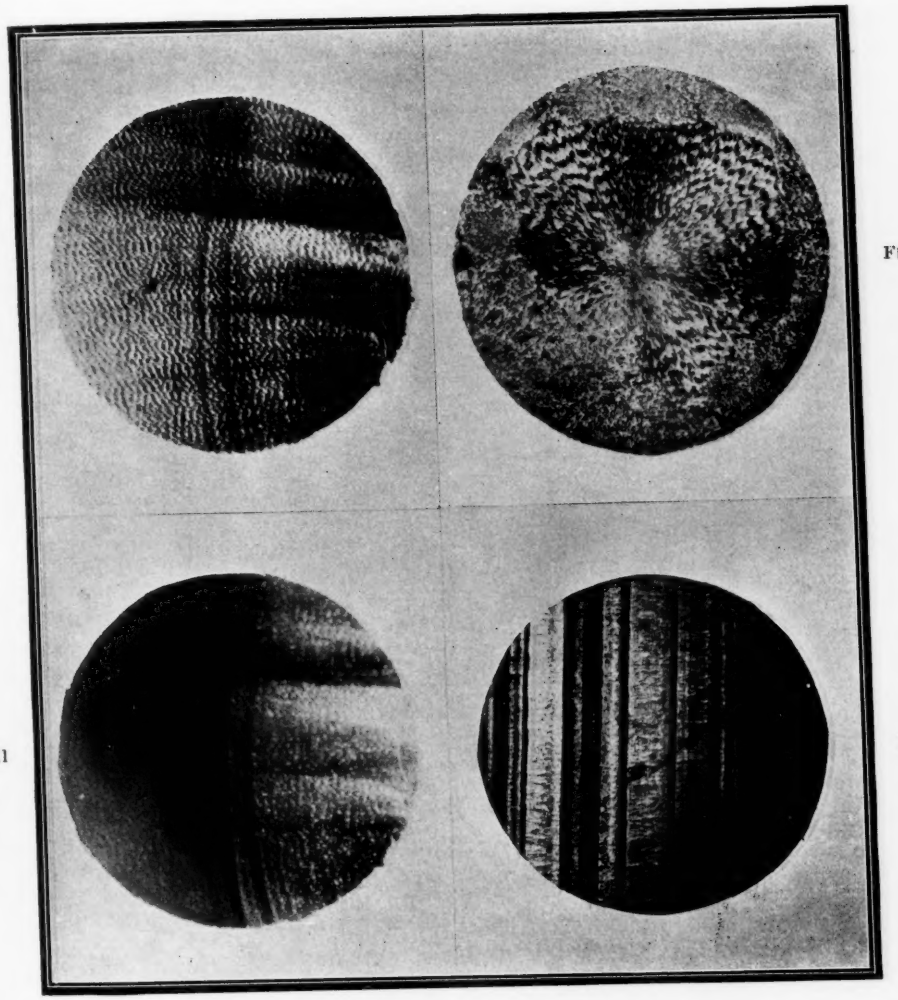


FIG. 9

FIG. 10

FIG. 11

FIG. 12

FIG. 13

FIG. 14

FIG. 15

variation in the orientation of the *c*-axes of the crystallites in the successive layers which are perpendicular to the length of the fibres.

Confirmation of the ideas regarding the structure of the material as deduced from its optical behaviour is forthcoming when the X-ray patterns of chalcedony are recorded for different regions and interpreted. In Figs. 13, 14 and 15 appearing in Plate XXXVI the X-ray patterns are reproduced. Fig. 13 is the record for a region exhibiting transparency and Figs. 14 and 15 are the records for areas exhibiting greater opacity. The X-ray pattern reproduced in Fig. 13 demonstrates that the crystallites of quartz composing the material are orientated with their *a*-axes common.

In conclusion the author wishes to express his grateful thanks to Professor Sir C. V. Raman, F.R.S., N.L., for suggesting the problem and for the valuable help and inspiring guidance that he offered during the course of this investigation.

6. Summary

Common chalcedony and agate, when examined by methods of investigation similar to that employed in the case of iridescent agate, the results of which have already been reported in these *Proceedings*, exhibit analogous features. The transmission and diffusion of light, their polarisation characters and the influence of the thickness of the medium on these features are discussed from a theoretical standpoint. The results are borne out by observations made with several specimens of agate and chalcedony. The lamellar structure which is often exhibited by chalcedony is found to arise from the orientation of the *c*-axes of the crystallites of quartz in the fibres along the banding planes which run transversely to the former. X-ray patterns of chalcedony in such regions reveal that the crystallites of quartz are orientated with their *a*-axes common along the fibre length.

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ON A CLASS OF STOCHASTIC INTEGRO-DIFFERENTIAL EQUATIONS

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SUMMARY

The solutions of the stochastic integro-differential equation involving, in addition to the random transitions of the stochastic variable, a deterministic change, are obtained under various approximations. It is shown that the solution in the case of a negative deterministic change is strikingly different from the solution when the change is positive. Examples from physics and astro-physics are cited to illustrate such stochastic processes.

THE following type of process is well known in the theory of stochastic processes.

$\pi(E|E_0, t)\,dE$ is the probability that the continuous stochastic variable $E(t)$ assumes a value between E and $E + dE$ at t (t is a one-dimensional parameter with respect to which the process progresses), given that it had the value E_0 at $t = 0$. We assume the process is homogeneous and Markovian with respect to t. We are given that:

$R(E'|E)\,dE'dt$ is the probability that the stochastic variable jumps from E to an interval between E' and $E' + dE'$ in the parametric interval dt. $R(E'|E) = 0$ if $E' > E$.

The stochastic integro-differential equation for the above process can be directly written down using its Markovian character

$$\frac{\partial\pi(E|E_0, t)}{\partial t} = -\pi(E|E_0, t)\int_0^E R(E'|E)\,dE' + \int_E^\infty \pi(E'|E_0, t) \times R(E|E')\,dE'. \qquad (1)$$

In some physical problems we may have to deal with stochastic processes more complicated than the one described above. In this paper, we shall deal with two types of complications.

I. In addition to the transition process defined by $R(E'|E)$ we are given that $\pm\beta(E)\,dt$, β being always positive, is the deterministic change

in the stochastic variable in interval dt if it has the value E at t. The positive sign before β denotes an increment and a negative sign, a loss. In such a case, the stochastic integro-differential equation is given by*

$$\frac{\partial \pi (E|E_0, t)}{\partial t} \pm \frac{\partial}{\partial E}\left\{\beta \pi (E|E_0, t)\right\} = -\pi (E|E_0, t) \int_0^E R (E'|E)\, dE' + \int_0^\infty \pi (E'|E_0, t)\, R (E|E')\, dE' \quad (2)$$

We write $+ \frac{\partial}{\partial E}[\beta \pi (E|E_0, t)]$ when we deal with an increment and $- \frac{\partial}{\partial E}[\beta \pi (E|E_0, t)]$ when we deal with a loss.

This process will be dealt with in Part I of this paper.

II. We assume $R (E'|E) = 0$ if $E < \nu$. In such a case, equation (1) splits up into two equations. This process, we shall consider in Part II of this paper.

Physical examples of the above process can be cited.

Equation (1) is useful in describing the energy loss of fast particles due to radiation. Equation (2) with $+\beta$ is the fundamental equation of the astrophysical problem of the fluctuations in brightness of the Milky Way. Equation (2) with $-\beta$ has not been solved explicitly and the main contribution in this paper is *to obtain the solution in this case from the solution for the case* $+\beta$. Such a process arises where we take ionisation loss also into account when fast particles passing through matter lose energy by radiation.

The complication of Type II arises in the case of the energy distribution of recoil atoms in liquids, a problem considered in Part II.

Before we deal with the actual problems, we shall obtain the formal solution of (2) [which includes that of (1)] assuming that (i) $R (E'|E)\, dE'$ can be written as $R (q)\, dq$ where $q = E'/E$, $R (q) = 0$ for $q > 1$ or $q < 0$, and (ii) $\beta (E) = \beta E^k H (E)$ where k is a non-negative integer and $H (E)$ is the Heaviside unit function, *i.e.*, $H (E) = 1$ if $E > 0$ and $H (E) = 0$ if $E < 0$. This only means that in our stochastic process E can take only non-negative values.

We now reduce (2) to a differential equation by the use of a Mellin's transformation.

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* For the derivation of this equation see, for example, Alladi Ramakrishnan (1952).

Defining

$$p(s, t) = \int_0^\infty \pi(E|E_0, t)\, E^{s-1}\, dE,$$

$$\omega(s) = \int_0^1 R(q)\, q^{s-1}\, dq, \quad \alpha = \omega(1) = \int_0^1 R(q)\, dq \tag{3}$$

we get

$$\frac{\partial p(s, t)}{\partial t} = -\alpha p(s, t) + \omega(s)\, p(s, t) \pm \beta(s-1)\, p(s+k-1, t) \tag{4}$$

with the initial conditions,

$$\pi(E|E_0, 0) = \delta(E - E_0) \qquad i.e., p(s, 0) = E_0^{s-1} \tag{5}$$

where δ is the Dirac delta-function.

When $\beta = 0$ the above equation can be directly solved.

$$p(s, t) = E_0^{s-1}\, e^{\{\omega(s)-\alpha\}t} \tag{6}$$

and $\pi(E|E_0, t)$ is obtained by inversion.

$$\pi(E|E_0, t) = \frac{1}{2\pi i E_0} \int_{\sigma-i\infty}^{\sigma+i\infty} \left(\frac{E_0}{E}\right)^s e^{\{\omega(s)-\alpha\}t}\, ds. \tag{7}$$

When $k = 1$ and $\beta \neq 0$, the equation can be solved easily. The solution is

$$\pi(E|E_0, t) = \frac{1}{2\pi i E_0} \int_{\sigma-i\infty}^{\sigma+i\infty} \left(\frac{E_0}{E}\right)^s e^{\{\omega(s)-\alpha\pm(s-1)\beta\}t}\, ds.$$

PART I

Let us take the case when $k = 0$, $\beta \neq 0$. Then we are faced with a difference equation in a complex variable which obviously cannot be solved by simple iteration. We shall show that in the special case of $R(q') = \delta(q' - q)$, the equation can be completely solved. The solution when βdt represents a deterministic increment was first obtained by Chandrasekhar and Munch (1950, 51) in connection with a stochastic problem in astrophysics and subsequently by one of us using different methods (Ramakrishnan, 1953). The solutions are strikingly different in the two cases of deterministic gain and loss and our object is to discuss the two, and study their behaviour as t tends to infinitity.

Before we do so, it is necessary to note that $\alpha = \int_0^1 R(q)\, dq$ is independent of q and αdt represents the probability that a discrete jump occurs in dt.

The number of discrete jumps in an interval t has a Poisson distribution given by

$$e^{-\alpha t}(\alpha t)^n/n\,! \tag{8}$$

We can define $\pi_n(\mathrm{E}|\mathrm{E}_0, t)\,d\mathrm{E}$ to be the joint probability that n events have occurred and the variable has a value between E and $\mathrm{E}+d\mathrm{E}$ given that it had a value E_0 at $t=0$.

Then

$$\pi_n(\mathrm{E}|\mathrm{E}_0, t) = \frac{e^{-\alpha t}(\alpha t)^n}{n\,!}\,\pi(\mathrm{E}|\mathrm{E}_0, n, t) \tag{9}$$

where $\pi(\mathrm{E}|\mathrm{E}_0, n, t)$ is the conditional probability that the variable lies between E and $\mathrm{E}+d\mathrm{E}$ given that n discrete transitions have occurred. The stochastic variable in the case of $\pi_n(\mathrm{E}|\mathrm{E}_0, t)$ when βdt denotes an increment is obviously

$$\begin{aligned}\mathrm{E} &= \mathrm{E}_0 q^n + x_1 q^{n-1} + (x_2 - x_1)\,q^{n-2} + \ldots + (x_n - x_{n-1})\,q + (t - x_n)\\ &= \mathrm{E}_0 q^n + \mathrm{X}\end{aligned} \tag{10}$$

where we assume that the n discrete transitions occur between x_1 and $x_1 + dx_1$, x_2 and $x_2 + dx_2, \ldots$, x_n and $x_n + dx_n$ respectively. X is the stochastic variable in $\pi_n(\mathrm{E}|\mathrm{E}_0, t)$ when $\mathrm{E}_0 = 0$. The distribution function of X has been obtained by Chandrasekhar and Munch* (β can be put equal to unity without loss of generality).

$$\begin{aligned}\pi_n(\mathrm{E}, t) &= -\frac{\alpha^n e^{-\alpha t}}{(n-1)\,!}\sum_{k=0}^{m-1} \mathrm{A}_k{}^n\,(\mathrm{E} - tq^k)^{n-1},\ (tq^m < \mathrm{E} < tq^{m-1})\\ \pi_0(\mathrm{E}, t) &= e^{-\alpha t}\,\delta(\mathrm{E} - t).\end{aligned} \tag{11}$$

where

$$\mathrm{A}_k{}^n = \frac{1}{(q^n - q^k)(q^{n-1} - q^k)\ldots(q^{k+1} - q^k)(q^{k-1} - q^k)(q^{k-2} - q^k)\ldots(1 - q^k)}.$$

We can immediately extend the above solution to the case when $\mathrm{E}_0 \neq 0$

$$\begin{aligned}\pi_n(\mathrm{E}|\mathrm{E}_0, t) &= -\frac{\alpha^n e^{-\alpha t}}{(n-1)\,!}\sum_{k=0}^{m-1} \mathrm{A}_k{}^n\,(\mathrm{E} - \mathrm{E}_0 q^n - tq^k)^{n-1},\\ &\qquad (tq^m < \mathrm{E} - \mathrm{E}_0 q^n < tq^{m-1})\\ \pi_0(\mathrm{E}|\mathrm{E}_0, t) &= e^{-\alpha t}\,\delta(\mathrm{E} - \mathrm{E}_0 - t);\ \pi(\mathrm{E}|\mathrm{E}_0, t) = \sum_{n=0}^{\infty}\pi_n(\mathrm{E}|\mathrm{E}_0, t).\end{aligned} \tag{12}$$

We note that the solution is continuous in the range $0 \leqslant \mathrm{E} < \mathrm{E}_0 + t$ and at $\mathrm{E} = t + \mathrm{E}_0$, there is a delta-function singularity.

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* We give here the solution in the form obtained by one of us (R) in a subsequent paper: *Proc. Camb. Phil. Soc.*, 1953, **49**, 473. When $\mathrm{E}_0 = 0$, we write $\pi_n(\mathrm{E}|\mathrm{E}_0, t)$ as $\pi_n(\mathrm{E}, t)$.

Now consider the case when βdt represents deterministic loss. Then our stochastic variable is obviously

$$\begin{aligned} \mathrm{E} &= \mathrm{E}_0 q^n - x_1 q^{n-1} - (x_2 - x_1)\, q^{n-2} - \cdots - (x_n - x_{n-1})\, q - (t - x_n) \\ &= \mathrm{E}_0 q^n - \mathrm{X} \end{aligned} \tag{13}$$

Compare (13) with (10). While in (10) the variable is the sum of two stochastic variables which can assume only positive values, in (13) it is the difference between two variables which can assume only positive values. If the physical conditions of the problem require that E should be non-negative then the probability that E should be exactly zero is given by the probability that X is greater than $\mathrm{E}_0 q^n$, *i.e.*, at $\mathrm{E} = 0$, there is a delta-function singularity. This feature is not present in the case of deterministic gain. The difference will be apparent if we take two stochastic variables x and y which can assume only non-negative values and form the stochastic variable $z = x + y$. If $\mathrm{D}_1(x)$, $\mathrm{D}_2(y)$, $\mathrm{D}_3(z)$ are the distribution functions of x, y and z respectively, then

$$\mathrm{D}_3(z) = \int_0^z \mathrm{D}_1(x)\, \mathrm{D}_2(z - x)\, dx, \quad \bar{z} = \bar{x} + \bar{y} \tag{14}$$

where $\bar{x}$, $\bar{y}$, $\bar{z}$ are the mean values of x, y, z, respectively.

If $z = x - y$, then

$$\mathrm{D}_3(z) = \int_0^\infty \mathrm{D}_1(y + z)\, \mathrm{D}_2(y)\, dy \tag{15}$$

and

$$\bar{z} = \bar{x} - \bar{y} \tag{16}$$

But if we impose the condition that z must always be positive, then $\bar{z} \neq \bar{x} - \bar{y}$ *and there is a delta-function singularity for* $\mathrm{D}_3(z)$ at $z = 0$. The probability that z is equal to 0 is

$$\int_{-\infty}^0 \mathrm{D}_3(z)\, dz$$

where $\mathrm{D}_3(z)$ is given by (15)

$$\bar{z} = \bar{x} - \bar{y} + \int_0^\infty z \mathrm{D}_3(-z)\, dz = \int_0^\infty z\, \mathrm{D}_3(z)\, dz. \tag{17}$$

Hence our solution in the case of loss is given by

$$\pi_n(\mathrm{E}|\mathrm{E}_0, t) = -\frac{a^n e^{-at}}{(n-1)!} \sum_{k=0}^{m-1} \mathrm{A}_k{}^n (\mathrm{E}_0 q^n - \mathrm{E} - tq^k)^{n-1}, \quad (tq^m < \mathrm{E}_0 q^n - \mathrm{E} < tq^{m-1}) \tag{18}$$

The probability that $E = 0$ and n discrete transitions have occurred is given by†

$$P(0, n, t) = \int_{E_0 q^n}^{E_0} \pi_n(E, t)\, dE \quad \text{where } \pi_n(E, t) \text{ is given by (11)}$$

$$P(0, t) = \sum_{n=0}^{\infty} P(0, n, t) \tag{19}$$

where $P(0, t)$ represents the probability that $E = 0$ at t.

An example of a stochastic process involving deterministic gain is the astrophysical problem of "Fluctuations in Brightness of the Milky Way" so fully discussed by Chandrasekhar and Munch. As t tends to infinity, $\pi(E|E_0, t)$ has a stationary distribution which can be shown to be

$$\pi(E|E_0, t) \text{ as } t \to \infty, \ = \pi(E, t) \text{ as } t \to \infty, \ = \pi(E)$$

where

$$\pi(E) = \frac{d}{dE}\left[K e^{-E} \sum_{n=0}^{\infty} Q_n\, e^{-(1-q^n)E/q^n} \right], \tag{20}$$

$$K = \frac{1}{\prod_{i=1}^{\infty}(1 - q^i)}$$

and

$$Q_n = (-1)^n \prod_{r=1}^{n} \frac{q^r}{1 - q^r}$$

a solution obtained by Chandrasekhar and Munch. In the case of deterministic loss the stationary solution is trivial, and for all $t > E_0$, $\pi(E|E_0, t) = 0$ for all $E > 0$ and $P(0, t) = 1$. This is the direct result of the restrictive condition that $E = E_0 q^n - X$ must always be positive.

A direct example of the above process is the energy loss of fast particles when passing through matter. The discrete loss occurs due to the radiation, *i.e.*, Bremmstrahlung, while the steady deterministic loss occurs due to ionisation. $R(q)\, dq$ is given by the Bethe-Heitler cross-sections, but here we have made the approximation $R(q') = \delta(q' - q)$. But (19) represents the rigorous solution based upon the above assumption and $\frac{\partial P(0, t)}{\partial t}\, dt$ represents the probability that the energy of the particle assumes the value zero for the first time between t and $t + dt$. Hence $\frac{\partial P(0, t)}{\partial t}$ is the distribution function of the range of the particle.

† The actual numerical values for $P(0, t)$ for various values of t and q will be given in a later note.

PART II

We shall take the case when $\beta = 0$ but impose the following condition on $R(E'|E)\,dE'$. While $R(E'|E)\,dE'$ can be expressed as $R(q)\,dq$ where $q = E'/E$, $R(E'|E) = 0$ if $E < \nu$, *i.e.*, the discrete process is "frozen" when $E < \nu$. This splits the equation (1) into two and defining

$$\pi^{(2)}(E|E_0, t) = \pi(E|E_0, t) \qquad \text{if } E > \nu,$$

$$\pi^{(1)}(E|E_0, t) = \pi(E|E_0, t) \qquad \text{if } E < \nu$$

we obtain the equations

$$\frac{\partial \pi^{(2)}(E|E_0, t)}{\partial t} = -\pi^{(2)}(E|E_0, t)\,\alpha(E) + \int_E^{E_0} \pi^{(2)}(E'|E_0, t)\,R(E|E')dE', \quad (E > \nu)$$

$$\frac{\partial \pi^{(1)}(E|E_0, t)}{\partial t} = \int_\nu^{E_0} \pi^{(2)}(E'|E_0, t)\,R(E|E')\,dE', \quad (E < \nu). \tag{21}$$

If

$$\mathbf{R}(t) = \int_0^\epsilon \pi^{(1)}(E|E_0, t)\,dE$$

$$= \int_0^\epsilon dE \int_\nu^{E_0} R(E|E')\,dE' \int_0^t \pi^{(2)}(E'|E_0, t)\,dt \tag{22}$$

$\mathbf{R}(t)$ represents the probability that the stochastic variable assumes a value less than ϵ in time t. Let us obtain $\mathbf{R}(t)$ as t tends to infinity. It is quite clear that as $t \to \infty$

$$\pi^{(2)}(E|E_0, t) \to 0, \qquad (E > \nu) \tag{23}$$

$$\int_0^\nu \pi^{(1)}(E|E_0, t)\,dE \to 1, \quad (E < \nu). \tag{24}$$

We define

$$\Psi(E) = \int_0^\infty \pi^{(2)}(E|E_0, t)\,dt \tag{25}$$

$$\pi^{(1)}(E|E_0, \infty) = \int_\nu^{E_0} \Psi(E')\,R(E|E')\,dE' \tag{26}$$

$$\therefore \quad \mathbf{R} = \mathbf{R}(\infty) = \int_0^\epsilon \pi^{(1)}(E|E_0, \infty)\,dE \tag{27}$$

The Solution of the Problem

We shall solve equations (1) and (21) when $R(E|E')\,dE$ is homogeneous in E, E′, *i.e.*, $R(E|E')\,dE = R(q)\,dq$, $q = E/E'$ by defining the Mellin's transformations,

$$p(s, t) = \int_0^\infty \pi(E|E_0, t)\, E^{s-1}\, dE, \quad \omega_s = \int_0^1 R(q)\, q^{s-1}\, dq \tag{28}$$

Equation (1) reduces to (putting without loss of generality, $\alpha = 1$)

$$\frac{\partial p(s, t)}{\partial t} = -\, p(s, t)\,(1 - \omega_s); \quad p(s, 0) = E_0{}^{s-1} \tag{29}$$

$$p(s, t) = E_0{}^{s-1}\, e^{-(1-\omega_s)t} \tag{30}$$

$$\int_0^t p(s, t)\, dt = \frac{E_0{}^{s-1}}{1 - \omega_s}\,(1 - e^{-(1-\omega_s)t}) \tag{31}$$

$$\int_0^\infty p(s, t)\, dt = \frac{E_0{}^{s-1}}{1 - \omega_s} \tag{32}$$

$$\Psi(E) = \int_0^\infty \pi(E|E_0, t)\, dt = \frac{1}{2\pi i E_0} \int_{\sigma-i\infty}^{\sigma+i\infty} \frac{(E_0/E)^{s-1}}{1 - \omega_s}\, ds. \tag{33}$$

We shall now assume

$$R(E|E')\,dE = \frac{dE}{E'(1 - r)},\ R(E|E') = 0 \text{ only if } E' > E > E'r. \tag{34}$$

Thus

$$\omega_s = \int_r^1 q^{s-1}\, \frac{dq}{1 - r} = \frac{1 - r^s}{s(1 - r)}. \tag{35}$$

Expressing $\dfrac{1}{1 - \omega_s}$ as the infinite series $\sum_{m=0}^{\infty} \omega_s{}^m$ we get

$$\Psi(E) = \frac{1}{2\pi i E_0} \int_{\sigma-i\infty}^{\sigma+i\infty} \left(a^s \sum_{m=0}^{\infty} \omega_s{}^m \right) ds \text{ where } a = \frac{E_0}{E} \tag{36}$$

Substituting for ω_s from (35) and expanding $(1 - r^s)^m$ as a binomial series,

$$\Psi(E) = \frac{1}{2\pi i E_0} \int_{\sigma-i\infty}^{\sigma+i\infty} \left[a^s \sum_{m=0}^{\infty} \frac{1}{s^m (1 - r)^m} \sum_{j=0}^{m} (-1)^j \binom{m}{j} r^{sj} \right] ds \tag{37}$$

Now

$$\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty}\frac{a^s r^{sj}}{s^m}\,ds=\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty}\frac{e^{s\log ar^j}}{s^m}\,ds \tag{38}$$

We know

$$\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty}\frac{e^{sz}}{s^m}\,ds=\frac{z^{m-1}}{(m-1)\,!}\quad\text{if } z>0 \tag{39}$$

and is equal to zero if $z<0$,

so that the contour integral in (38) is equal to

$$\frac{(\log ar^j)^{m-1}}{(m-1)\,!}\quad\text{if } ar^j>1,\ i.e.,\ \mathrm{E}<\mathrm{E}_0 r^j \tag{40}$$

and to zero if $\mathrm{E}>\mathrm{E}_0 r^j$.

Hence, if $\mathrm{E}_0 r^{l-1}>\mathrm{E}>\mathrm{E}_0 r^l$ the expression (37) for $\Psi(\mathrm{E})$, on integration, splits up into two parts, for the contour integral in it vanishes for $j\geqslant l$.

Thus

$$\Psi(\mathrm{E})=\frac{1}{\mathrm{E}_0}\sum_{m=0}^{l-1}\sum_{j=0}^{m}\frac{(-1)^j\binom{m}{j}(\log ar^j)^{m-1}}{(m-1)\,!\,(1-r)^m}+\frac{1}{\mathrm{E}_0}\sum_{m=l}^{\infty}\sum_{j=0}^{l-1}\frac{(-1)^j\binom{m}{j}(\log ar^j)^{m-1}}{(m-1)\,!\,(1-r)^m} \tag{41}$$

Putting $(\log ar^j)^{m-1}$ as $(\log a+j\log r)^{m-1}$ and expanding as a binomial series, the first part of expression (41) for $\Psi(\mathrm{E})$ can be put in such a form that by identity (A 16) (*see* Appendix) it can be shown to vanish.

Hence

$$\Psi(\mathrm{E})=\frac{1}{\mathrm{E}_0}\sum_{m=l}^{\infty}\sum_{j=0}^{l-1}\frac{(-1)^j\binom{m}{j}\left(\log\frac{\mathrm{E}_0 r^j}{\mathrm{E}}\right)^{m-1}}{(m-1)\,!\,(1-r)^m}. \tag{42}$$

This expression can be substituted in (26)

$$\pi^{(1)}(\mathrm{E}|\mathrm{E}_0,\infty)=\int_{\mathrm{E}}^{\mathrm{E}/r}\Psi(\mathrm{E}')\frac{d\mathrm{E}'}{\mathrm{E}'(1-r)}. \tag{43}$$

In this integration, because of the discontinuities of the function $\Psi(E)$ as given by (42), two distinct cases arise.

Let

$$E_0 r^{k-1} > \nu > E_0 r^k. \tag{44}$$

Case I. $E_0 r^k > E > E_0 r^{k+1}$

The whole range of integration ν to $\frac{E}{r}$ being in the same domain $\left(E_0 r^{k-1} > \frac{E}{r} > \nu > E_0 r^k\right)$ direct integration is possible, and we have

$$\pi^{(1)}(E|E_0, \infty) = \int_{\nu}^{E/r} \sum_{m=k}^{\infty} \sum_{j=0}^{k-1} \frac{(-1)^j \binom{m}{j} \left(\log \frac{E_0}{E'} r^j\right)^{m-1}}{E_0 (m-1)\,!\,(1-r)^m} \frac{dE'}{E'(1-r)}$$

$$= \frac{1}{E_0(1-r)} \sum_{j=0}^{k-1} \sum_{m=k}^{\infty} \frac{(-1)^j \binom{m}{j}}{m!\,(1-r)^m} \left[\left(\log \frac{E_0 r^j}{\nu}\right)^m - \left(\log \frac{E_0 r^{j+1}}{E}\right)^m\right], \quad (E_0 r^k > E > E_0 r^{k+1}). \tag{45}$$

Case II. $\nu > E > E_0 r^k$

The range of integration being in two different domains, the discontinuity of $\Psi(E)$ necessitates separate integration for the two parts.

Thus

$$\pi^{(1)}(E|E_0, \infty) = \int_{\nu}^{E_0 r^{k-1}} \sum_{j=0}^{k-1} \sum_{m=k}^{\infty} \frac{(-1)^j \binom{m}{j} \left(\log \frac{E_0 r^j}{E'}\right)^{m-1}}{E_0 (m-1)!\,(1-r)^m} \frac{dE'}{E'(1-r)}$$

$$+ \int_{E_0 r^{k-1}}^{E/r} \sum_{j=0}^{k-2} \sum_{m=k-1}^{\infty} \frac{(-1)^j \binom{m}{j} \left(\log \frac{E_0 r^j}{E'}\right)^{m-1}}{E_0 (m-1)!\,(1-r)^m} \times \frac{dE'}{E'(1-r)} \tag{46}$$

which gives

$$\pi^{(1)}(E|E_0, \infty) = \frac{1}{E_0(1-r)} \sum_{j=0}^{k-1} \sum_{m=k}^{\infty} \frac{(-1)^j \binom{m}{j}}{m!(1-r)^m} \left[\left(\log \frac{E_0 r^j}{\nu} \right)^m - \left((j-k+1) \log r \right)^m \right] + \frac{1}{E_0(1-r)} \times \sum_{j=0}^{k-2} \sum_{m=k-1}^{\infty} \frac{(-1)^j \binom{m}{j}}{m!(1-r)^m} \left[\left((j-k+1) \log r \right)^m - \left(\log \frac{E_0 r^{j+1}}{E} \right)^m \right] \quad (47)$$

This can be reduced to

$$\pi^{(1)}(E|E_0, \infty) = \frac{1}{E_0(1-r)} \sum_{j=0}^{k-1} \sum_{m=k}^{\infty} \frac{(-1)^j \binom{m}{j}}{m!(1-r)^m} \left(\log \frac{E_0 r^j}{\nu} \right)^m - \frac{1}{E_0(1-r)} \sum_{j=0}^{k-2} \sum_{m=k-1}^{\infty} \frac{(-1)^j \binom{m}{j}}{m!(1-r)^m} \times \left(\log \frac{E_0 r^{j+1}}{E} \right)^m + \frac{(-1)^{k-1}}{E_0(1-r)} \frac{(\log r)^{k-1}}{(1-r)^{k-1}}, \quad (\nu > E > E_0 r^k). \quad (48)$$

In making this reduction, identities (A 16) and (A 17) (*see* Appendix) have been used.

Equations (45) and (48) can be put in a more useful form by considering the infinite sum over m as an exponential function minus a finite sum. Then they become

$$\pi^{(1)}(E|E_0, \infty) = \frac{1}{E_0(1-r)} \sum_{j=0}^{k-1} \frac{(-1)^j}{j!} \left(\frac{\log E_0 r^j/\nu}{1-r} \right)^j \left[\left(\frac{E_0 r^j}{\nu} \right)^{\frac{1}{1-r}} - \sum_{m=0}^{k-j-1} \frac{1}{m!} \left(\frac{\log E_0 r^j/\nu}{1-r} \right)^m \right] - \frac{1}{E_0(1-r)}$$

$$\times \sum_{j=0}^{k-1} \frac{(-1)^j}{j!} \left(\frac{\log E_0 r^{j+1}/E}{1-r}\right)^j \left[\left(\frac{E_0 r^{j+1}}{E}\right)^{\frac{1}{1-r}} - \sum_{m=0}^{k-j-1} \frac{1}{m!} \left(\frac{\log E_0 r^{j+1}/E}{1-r}\right)^m\right], (E_0 r^k > E > E_0 r^{k+1}) \tag{49}$$

and

$$\pi^{(1)}(E|E_0, \infty) = \frac{1}{E_0(1-r)} \sum_{j=0}^{k-1} \frac{(-1)^j}{j!} \left(\frac{\log E_0 r^j/\nu}{1-r}\right)^j \left[\left(\frac{E_0 r^j}{\nu}\right)^{\frac{1}{1-r}} - \sum_{m=0}^{k-j-1} \frac{1}{m!} \left(\frac{\log E_0 r^j/\nu}{1-r}\right)^m\right] - \frac{1}{E_0(1-r)}$$

$$\times \sum_{j=0}^{k-2} \frac{(-1)^j}{j!} \left(\frac{\log E_0 r^{j+1}/E}{1-r}\right)^j \left[\left(\frac{E_0 r^{j+1}}{E}\right)^{\frac{1}{1-r}} - \sum_{m=0}^{k-j-2} \frac{1}{m!} \left(\frac{\log E_0 r^{j+1}/E}{1-r}\right)^m\right] + \frac{(-1)^{k-1}}{E_0(1-r)}$$

$$\times \frac{(\log r)^{k-1}}{(1-r)^{k-1}}, \ (\nu > E > E_0 r^k) \tag{50}$$

Again using identities (A 16) and (A 17) after putting the finite sums over m in the two expressions in a suitable form, we find that (49) and (50) reduce to

$$\pi^{(1)}(E|E_0, \infty) = \frac{1}{E_0(1-r)} \sum_{j=0}^{k-1} \frac{(-1)^j}{j!} \left(\frac{E_0 r^j}{\nu}\right)^{\frac{1}{1-r}} \left(\frac{\log E_0 r^j/\nu}{1-r}\right)^j$$

$$- \frac{1}{E_0(1-r)} \sum_{j=0}^{k-1} \frac{(-1)^j}{j!} \left(\frac{(E_0 r^{j+1}}{E}\right)^{\frac{1}{1-r}}$$

$$\times \left(\frac{\log E_0 r^{j+1}/E}{1-r}\right)^j, (E_0 r^k > E > E_0 r^{k+1}) \tag{51}$$

and

$$\pi^{(1)}(E|E_0, \infty) = \frac{1}{E_0(1-r)} \sum_{j=0}^{k-1} \frac{(-1)^j}{j!} \left(\frac{E_0 r^j}{\nu}\right)^{\frac{1}{1-r}} \left(\frac{\log E_0 r^j/\nu}{1-r}\right)^j$$

$$- \frac{1}{E_0(1-r)} \sum_{j=0}^{k-2} \frac{(-1)^j}{j!} \left(\frac{E_0 r^{j+1}}{E}\right)^{\frac{1}{1-r}}$$

$$\times \left(\frac{\log E_0 r^{j+1}/E}{1-r}\right)^j, (\nu > E > E_0 r^k). \quad (52)$$

This is the probability distribution of the stochastic variable after the stationary state is attained. From expressions (51) and (52), the probability that the variable assumes a value less than ϵ can be calculated simply by integrating these expressions over E between the limits $r\nu$ (energies below which cannot be reached) and ϵ; or by substracting from unity, the integral of $\pi^{(1)}(E|E_0, \infty)$ over E between the limits ϵ and ν. Both these give identical values since the integral of $\pi^{(1)}(E|E_0, \infty)$ over the whole range $r\nu$ to ν is unity; but for convenience, (51) is integrated by the former method (because $r\nu$ and ϵ being in the same domain, no discontinuities occur in the region of integration), while (52) is integrated by the latter way (here ϵ, ν are in the same domain).

The integration is done easily by making the substitution, $\frac{1}{1-r} \log \frac{E_0 r^{j+1}}{E} = y$ when the integral assumes the form $\int e^{r\nu} y^j dy$ which can easily be evaluated.

Thus we get the probability **R** in the two cases:

$$\mathbf{R} = \frac{\epsilon - r\nu}{\nu(1-r)} \sum_{j=0}^{k-1} \frac{(-1)^j}{j!} \left(\frac{E_0 r^j}{\nu}\right)^{\frac{r}{1-r}} \left\{\log \left(\frac{E_0 r^j}{\nu}\right)^{\frac{r}{1-r}}\right\}^j$$

$$+ \sum_{j=0}^{k-1} \sum_{l=0}^{j} \frac{(-1)^{j-l}}{(j-l)!} \left[\left(\frac{E_0 r^{j+1}}{\epsilon}\right)^{\frac{r}{1-r}} \left\{\log \left(\frac{E_0 r^{j+1}}{\epsilon}\right)^{\frac{r}{1-r}}\right\}^{j-l}\right.$$

$$\left. - \left(\frac{E_0 r^j}{\nu}\right)^{\frac{r}{1-r}} \left\{\log \left(\frac{E_0 r^j}{\nu}\right)^{\frac{r}{1-r}}\right\}^{j-l}\right], (E_0 r^k > \epsilon > E_0 r^{k+1}) \quad (53)$$

and

$$\mathbf{R} = 1 - \frac{\nu - \epsilon}{\nu(1-r)} \sum_{j=0}^{k-1} \frac{(-1)^j}{j!} \left(\frac{E_0 r^j}{\nu}\right)^{\frac{r}{1-r}} \left\{\log\left(\frac{E_0 r^j}{\nu}\right)^{\frac{r}{1-r}}\right\}^j$$

$$- \sum_{j=0}^{k-2} \sum_{l=0}^{j} \frac{(-1)^{j-l}}{(j-l)!} \left[\left(\frac{E_0 r^{j+1}}{\nu}\right)^{\frac{r}{1-r}} \left\{\log\left(\frac{E_0 r^{j+1}}{\nu}\right)^{\frac{r}{1-r}}\right\}^{j-l}\right.$$

$$\left. - \left(\frac{E_0 r^{j+1}}{\epsilon}\right)^{\frac{r}{1-r}} \left\{\log\left(\frac{E_0 r^{j+1}}{\epsilon}\right)^{\frac{r}{1-r}}\right\}^{j-l}\right], (\nu > \epsilon > E_0 r^k) \qquad (54)$$

The above mathematical problem arose in connection with the theoretical treatment of the energy distribution of recoil atoms in liquids produced as a consequence of the emission of gamma-rays of substantial momentum due to the radio-active capture of neutrons by nuclei. The physical process, according to Libby, Miller and others (Libby, 1947; Miller, Gryder and Dodson, 1950; Capron and Oshima, 1952) can be briefly described as follows:

(i) Every (n, γ) process produces a free recoil atom with the same kinetic energy E_0. The kinetic energy of the atom is such that the atom cannot participate in stable chemical combination until it has lost energy.

(ii) Energy loss occurs by elastic "billiard ball collisions" with the solvent atoms.

(iii) If sufficient energy is transferred in a given collision the struck molecule will be dissociated into free radicals. In case the recoil atom has a kinetic energy less than a critical amount ϵ after this impact it will be trapped in a liquid cage of free radicals.

(iv) We assume that sufficient energy is not transferred if the energy is below a critical amount ν, $(\nu > \epsilon)$ to produce dissociation. *The effect of assumption (iv) is that only those atoms which 'drop' to an energy below ϵ from an energy state greater than ν, are 'trapped' while atoms with energy between ν and ϵ which drop to an energy below ϵ escape the cage and move freely.*

Our object is to find **R** the ratio of the trapped recoil atoms to the total number of recoil atoms in the stationary state. **R** is given by (53) and (54).

APPENDIX

We define coefficients $A_k{}^r$ ($r \geqslant k$ always) obeying the relations

$$A_k{}^n = \frac{A_k{}^{n-1}}{q_n - q_k} \tag{A 1}$$

$$A_k{}^k = -[A_0{}^k + A_1{}^k + \ldots\ldots + A_{k-1}{}^k], \quad A_0{}^0 = 1 \tag{A 2}$$

From (A 1) and (A 2)

$$(-1)^k A_k{}^k = -\left[\frac{A_0{}^0}{(q_0 - q_k)(q_0 - q_{k-1})\ldots\ldots(q_0 - q_1)} - \frac{A_1{}^1}{(q_1 - q_k)(q_1 - q_{k-1})\ldots\ldots(q_1 - q_2)} + \ldots\ldots + (-1)^{k-1}\frac{A_{k-1}{}^{k-1}}{q_{k-1} - q_k}\right] \tag{A 3}$$

Substituting in (A 3) for $A_{k-1}{}^{k-1}$ only, an expression similar to (A 3), and after reducing, substituting for $A_{k-2}{}^{k-2}$ alone and so on, by successive reduction we get

$$(-1)^k A_k{}^k = \frac{1}{(q_k - q_{k-1})(q_k - q_{k-2})\ldots\ldots(q_k - q_0)} \tag{A 4}$$

and

$$(-1)^n A_k{}^n = \frac{1}{(q_k - q_n)(q_k - q_{n-1})\ldots(q_k - q_{k+1})(q_k - q_{k-1})(q_k - q_{k-2})\ldots(q_k - q_0)} \tag{A 5}$$

The sum

$$\sum_{k=0}^{n} A_k{}^n q_k{}^m = \sum_{k=0}^{n} A_k{}^n (q_k{}^{m-1})(q_k - q_n) + q_n \sum_{k=0}^{n} A_k{}^n q_k{}^{m-1} \tag{A 6}$$

i.e.,

$$-\sum_{k=0}^{n} A_k{}^n q_k{}^m = \sum_{k=0}^{n-1} A_k{}^{n-1} q_k{}^{m-1} - q_n \sum_{k=0}^{n} A_k{}^n q_k{}^{m-1}$$

$$= \sum_{k=0}^{n-1} A_k{}^{n-1} q_k{}^{m-1} + q_n \sum_{k=0}^{n-1} A_k{}^{n-1} q_k{}^{m-2} + \ldots\ldots + q_n{}^{m-1} \sum_{k=0}^{n-1} A_k{}^{n-1}$$

$$= \sum_{r=0}^{m-1} K_r{}^1 \sum_{k=0}^{n-1} A_k{}^{n-1} q_k{}^{m-1-r} \quad \text{where} \quad K_r{}^1 = q_n{}^r \tag{A 7}$$

Using relation (A 6) this can be reduced to

$$-\sum_{r=0}^{m-2} K_r{}^2 \sum_{k=0}^{n-2} A_k{}^{n-2} q_k{}^{m-2-r}, \quad \text{where} \quad K_r{}^2 = \sum_{p=0}^{r} K_p{}^1 q_{n-1}{}^{r-p} \quad \text{(A 7 } a\text{)}$$

This can be further reduced so that in general, we can write

$$(-1)^i \sum_{k=0}^{n} A_k{}^n q_k{}^m = \sum_{r=0}^{m-i} K_r{}^i \sum_{k=0}^{n-i} A_k{}^{n-i} q_k{}^{m-i-r} \qquad \text{(A 8)}$$

where i may vary from 0 to m or n, whichever is smaller, and

$$K_r{}^i = K_r{}^{i-1} + K_{r-1}{}^i q_{n-i+1} \qquad \text{(A 9)}$$

from which we get

$$K_r{}^i = \sum_{p=0}^{i} K_{r-1}{}^p q_{n+1-p} \qquad \text{(A 10)}$$

and

$$K_r{}^i = \sum_{p=0}^{r} K_p{}^{i-1} q_{n-i+1}{}^{r-p} \qquad \text{(A 11)}$$

From (A 8), we see that if $m < n$, putting $i = m$ in the right-hand side of (A 8) it reduces to $K_0{}^m \sum_{k=0}^{m-n} (-1)^{m-n} A_k{}^{m-n}$ which is zero by (A 2). Hence

$$\sum_{k=0}^{n} A_k{}^n q_k{}^m = 0, \quad (m < n) \qquad \text{(A 12)}$$

When $m = n$, putting $i = m = n$ in (A 8), we get, since $K_0{}^i = 1$ for all i,

$$(-1)^n \sum_{k=0}^{n} A_k{}^n q_k{}^m = 1, \quad (m = n) \qquad \text{(A 13)}$$

For $m > n$, we can put $i = n$ which then gives

$$(-1)^n \sum_{k=0}^{n} A_k{}^n q_k{}^m = \sum_{r=0}^{m-n} K_r{}^n q_0{}^{m-n-r}, \quad (m > n). \qquad \text{(A 14)}$$

Relations (A 12) and (A 13) are of direct application in the problem we are considering, where the coefficients $A_k{}^n$ are of a particular form, with

$$q_k = k \text{ so that } (-1)^n A_k{}^n = \frac{(-1)^{n-k}}{(n-k)!\,k!} \qquad \text{(A 15)}$$

Thus we have as particular cases of (A 12) and (A 13),

$$\sum_{k=0}^{n} \frac{(-1)^{n-k}}{(n-k)!\,k!}\, k^m = 0 \qquad (m < n) \tag{A 16}$$

and

$$\sum_{k=0}^{n} \frac{(-1)^{n-k}}{(n-k)!\,k!}\, k^m = 1 \qquad (m = n) \tag{A 17}$$

(A 16) and (A 17) have been used directly in the problem.

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NUCLEAR REDUCTION OF ANTHOXANTHINS IN THE SIDE PHENYL NUCLEUS

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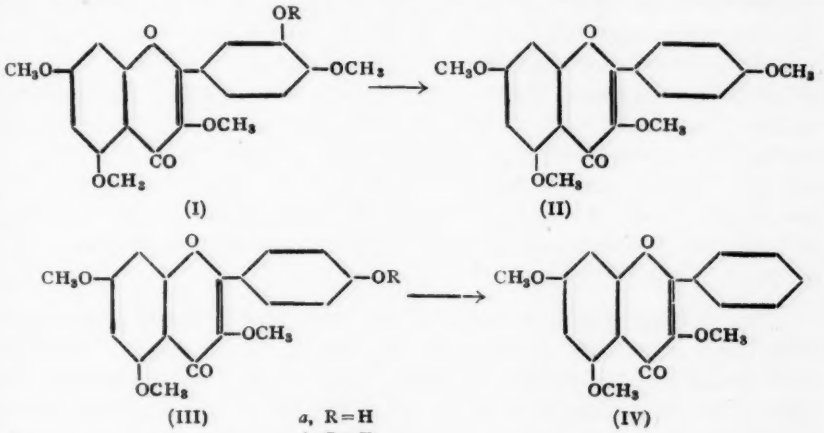
One of the implications of the theory of Robinson[1] relating to the biogenesis of anthocyanins and anthoxanthins was that members having the catechol unit in the side phenyl nucleus should represent the earliest stage. Support for this was provided by Lawrence, Price, Robinson and Robinson[2] from a detailed examination of the occurrence of anthocyanins. The data led to the conclusion that cyanidin is the primary member of the anthocyanidin group and the production of delphinidin (oxidation) and pelargonidin (reduction) involve one more stage in the evolution.

In view of the close relationship between anthocyanins and anthoxanthins, the above considerations should apply to the latter also. But here, the process of reduction should be considered to proceed further yielding compounds with no hydroxyl group in the side phenyl nucleus. These stages of reduction have not so far been carried out in the laboratory. As model experiments the nuclear reduction of O-tetramethylquercetin (I *a*) with a free hydroxyl group in the 3′-position has now been successfully done by the hydrogenolysis[3] of its tosyl ester (I *b*). The product is identical with



O-tetramethyl kæmpherol (II). Similarly the trimethyl ether of kæmpherol (III *a*) with a free hydroxyl group in the 4′-position has been converted into galangin trimethyl ether (IV). These results would indicate the possibility of nuclear reduction in the side phenyl nucleus of the flavonoids taking place in nature as mentioned above.

EXPERIMENTAL

3′-Tosyl quercetin tetramethyl ether and 4′-tosyl kæmpherol trimethyl ether

A dry acetone solution of quercetin tetramethyl ether[4] (I *a*) or kæmpherol trimethyl ether[5] (III *a*) (1 mole) was refluxed with tosyl chloride (1·1 mole) and anhydrous potassium carbonate (excess) for 3 hours. Acetone was distilled off and the potassium salts were dissolved in water when a crystalline solid separated out. It was filtered, washed with 5% aqueous sodium carbonate and then with water and dried. 3′-Tosyl quercetin tetramethyl ether (I *b*) crystallised from ethyl acetate-petroleum ether mixture as colourless rectangular rods and prismatic needles melting at 120–22° (Found: C, 59·9; H, 5·0. $C_{26}H_{24}O_9S$, $\frac{1}{2}$ H_2O requires C, 59·9; H, 4·8%). 4′-Tosyl kæmpherol trimethyl ether (III *b*) separated as colourless small rhombohedral plates melting at 280–81° after two crystallisations from alcohol (Found: C, 62·6; H, 5·3. $C_{25}H_{22}O_8S$ requires C, 62·3; H, 4·6%).

Reduction

Each of the above tosyl esters (1 g.) was dissolved in alcohol and Raney nickel (2 tea-spoonful) was suspended in the solution. A slow current of purified hydrogen gas was passed into this well-agitated suspension kept at room temperature (28° C.) for an hour. The mixture was filtered and the alcoholic solution concentrated. The nickel residue was treated with dilute hydrochloric acid, the product extracted with ether and the ether concentrate was mixed with the above alcoholic concentrate. The combined product was refluxed with 5% aqueous sodium carbonate (100 c.c.) for 2 hours and after cooling was extracted well with ether. The ether solution was concentrated when a colourless semi-solid mass separated. It was dried in a vacuum desiccator and crystallised from ethyl acetate-petroleum ether mixture. Yield, 0·1 g.

The 3′-tosyl quercetin tetramethyl ether (I *b*) yielded kæmpherol tetramethyl ether[6] (II) as colourless needles melting at 165–66° alone or when mixed with an authentic sample; while 4′-tosyl kæmpherol trimethyl ether (III *b*) gave galangin trimethyl ether[7] (IV) as colourless needles melting at 195–96° which was undepressed by admixture with a synthetic sample.

SUMMARY

By the application of nuclear reduction a quercetin derivative has been converted into kæmpherol and a kæmpherol derivative into galangin.

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NUCLEAR REDUCTION OF ANTHOXANTHINS

Complete Removal of Phenolic Hydroxyl Groups

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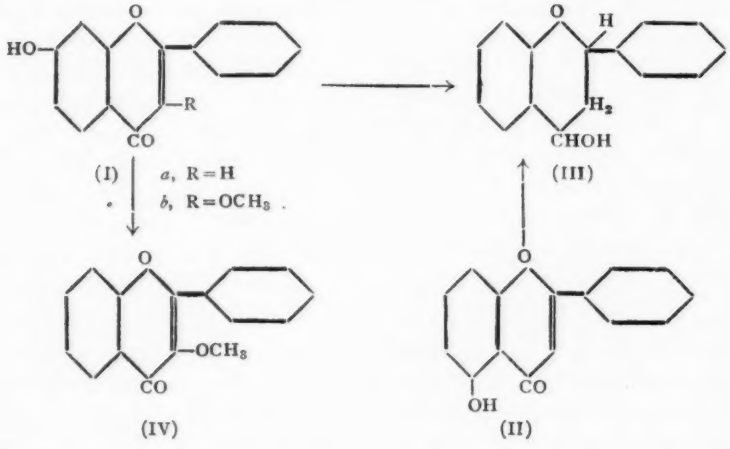
As compared with anthocyanins, a characteristic feature of anthoxanthins is the occurrence of complete nuclear reduction leading to the parent substance, flavone, which is found to occur free in plants. In previous communications[1] have been discussed the complete reduction in the side phenyl nucleus and the removal of a hydroxyl group from the 7 or 5-position of flavones. The removal of the final hydroxyl group in the condensed benzene ring has now been carried out. 7- or 5-Hydroxy flavone (I *a* and II) when tosylated and subjected to hydrogenolysis is found to yield a colourless product which could be identified as β-4-hydroxy-flavan (III). Obviously reduction has gone further than the removal of the tosyloxy group. The flavone first formed seems to be easily susceptible to reduction. From the results of all previous experiments on nuclear reduction in the flavone series, it is clear that the existence of a substituent either as hydroxyl or methoxyl gives stability to the flavone structure and the central γ-pyrone ring is left unreduced. But when all substituents are removed it seems to become susceptible to reduction. This conclusion has been supported by carrying



out the nuclear reduction of 3-methoxy-7-hydroxy flavone (I *b*). The product is found to be simple flavonol methyl ether (IV) which has escaped further hydrogenation. Incidentally these experiments provide a simple method of preparing the parent substance of the flavonol series.

Experimental

7-Tosyloxy flavone

7-Hydroxy flavone was prepared by the method of Robinson and Venkataraman[2] with the additional treatment with boiling aqueous sodium carbonate in order to remove 3-acyl group. It (2 g.) was refluxed with tosyl chloride (1·9 g.) in dry acetone solution (150 c.c.) in presence of anhydrous potassium carbonate (5 g.) for 3 hours. The solvent was distilled off and the residue treated with water. The solid product was collected and crystallised from alcohol when it separated as long rectangular prisms and rods melting at 159–60° (Found: C, 67·1; H, 3·9. $C_{22}H_{16}O_5S$ requires C, 67·3; H, 4·1%).

5-Tosyloxy flavone

5-Hydroxy flavone (II) was obtained by the method of Rao, Rajagopalan and Seshadri.[3] It was newly observed that pyridine was better than alcohol as solvent for deacylation and by its use the product was obtained more readily in a purer form. It was tosylated with excess of tosyl chloride (3 moles) using the potassium carbonate-acetone method and boiling the mixture till it gave no colour with ferric chloride (20 hours). The product crystallised from alcohol as colourless long rectangular tablets melting at 188–89° (Found: C, 67·1; H, 4·4.; $C_{22}H_{16}O_5S$ requires C, 67·3; H, 4·1%).

Hydrogenolysis of 7- and 5-tosyloxy flavones

A slow current of purified hydrogen gas was passed through an agitated alcoholic solution of 7- or 5-tosyloxy flavone (1 g.) containing Raney nickel (one tea-spoonful) at room temperature for an hour. The alcoholic solution (A) was decanted and the nickel residue after decomposition with dilute hydrochloric acid was extracted with ether. The ether concentrate was mixed with the alcoholic solution (A) and the solvents were completely removed. The resulting solid was refluxed with 5% aqueous sodium carbonate (100 c.c.) for 2 hours. After cooling it was extracted with ether. The residue left after evaporating the ether extract was crystallised from ether-petroleum ether mixture when a colourless crystalline solid melting at 142–43° was obtained. It was found to agree with β-4-hydroxy flavan (III) obtained earlier by Mozingo and Adkins[4] by the reduction of flavone with Raney nickel. The identity was confirmed by acetylating it with acetic anhydride

and fused sodium acetate. The acetate crystallised from dilute methyl alcohol as colourless needles melting at 97–98°. Karrer, Yen and Reichstein[5] gave the melting point of 98–99° for this acetate.

The above experiment was repeated with 7-tosyloxy flavone at a lower temperature (15°) and using a shorter period (40 minutes). The product obtained after treatment with sodium carbonate and ether extraction was dissolved in the minimum quantity of alcohol, treated with caustic potash (0·5 g.) and the resulting solution kept for 15 minutes at room temperature. After dilution with water it was extracted with ether and the ether solution evaporated. The residue crystallised from petroleum ether as colourless needles melting at 142–43°. It was identical with β-4-hydroxy flavan (III) obtained in the earlier experiment. The yield was however poorer than in the earlier experiment.

Reduction of 7-hydroxy-3-methoxy flavone

7-Hydroxy-3-methoxy flavone[6] (I *b*) was tosylated as in the case of 7-hydroxy flavone. The product crystallised from alcohol as pale yellow rhombic prisms melting at 132-33° (Found: C, 65·1; H, 4·1. $C_{23}H_{18}O_6S$ requires C, 65·4; H, 4·3%).

The above tosyl ester (1 g.) was subjected to hydrogenolysis for 1 hour at room temperature. The product obtained after treatment with sodium carbonate and ether extraction of the resulting solution was sticky in nature. It was kept in alcoholic potash (0·5 g. in 10 c.c.) for 7 minutes, diluted with water and extracted with ether. The residue left after evaporating the solvent crystallised from methyl alcohol as colourless very large rectangular prisms melting at 114–15° identical with 3-methoxy flavone as reported by Oyamada.[7] Yield, 0·3 g. The identity was confirmed by demethylation with hydriodic acid to flavonol which crystallised from ethyl acetate-petroleum ether mixture as pale yellow needles and rectangular plates melting at 168–69° identical with the one obtained by Kostanecki.[8]

When the above experiment was repeated at a lower temperature (15°) and for a shorter period (40 minutes) most of the original compound was recovered unchanged and only a very small amount of flavonol methyl ether (IV) was obtained.

SUMMARY

Nuclear reduction of 7-hydroxy and 5-hydroxy flavones yields β-4-hydroxy flavan whereas 3-methoxy-7-hydroxy flavone yields 3-methoxy flavone. The pyrone ring escapes further reduction if there should be a substituent.

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ANTHRAQUINONE AND ANTHRONE SERIES

Part XIV. 1-Amino-3-chloroanthraquinone

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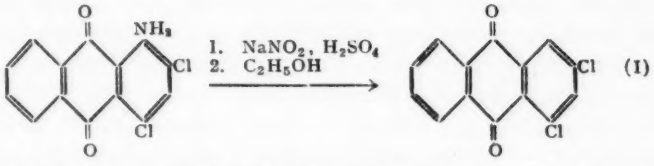
The methods described in the literature for the preparation of 1 : 3-dichloroanthraquinone (I) are (i) by the condensation of phthalic anhydride with *m*-dichlorobenzene in presence of aluminium chloride and cyclization of the dichlorobenzoylbenzoic acid with fuming sulphuric acid at 160°[1, 2]; (ii) by deamination of 2-amino-1 : 3-dichloroanthraquinone[3]; and (iii) by oxidation of 1 : 3 : 9 : 10-tetrachloroanthracene with chromic acid in acetic acid.[4] Since 1-amino-2 : 4-dichloroanthraquinone[5] is now readily available, its deamination offers a convenient route to 1 : 3-dichloroanthraquinone; a 95% yield has been obtained by boiling the diazonium sulphate from 1-amino-2 : 4-dichloroanthraquinone with ethanol in presence of a little copper sulphate.

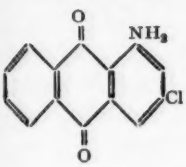


(I)

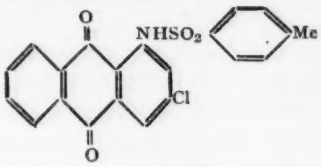
No reference to 1-amino-3-chloroanthraquinone (II) was available when this work was initiated, but according to a FIAT report[2] it is a valuable base for azoic dyeing, giving very bright shades with excellent fastness properties; combinations of the greatest interest were a scarlet with Naphtol AS-D, a red-brown with Naphtol AS-LT, and a red-yellow with Naphtol I3GH. Citing the FIAT report, Glassman[6] has stated: "In contrast to the pigments obtained by coupling diazotized α-aminoanthraquinone with naphthols, which are 'muddy' in shade, corresponding ones from 3-bromo- and 3-chloro-1-aminoanthraquinones give reds of a brightness comparable with that of Permanent Reds FRL to F4R. Light fastness is of a very high order, and some of the more outstanding properties are oil fastness and resistance to bleed (overstripe test)."

The base (II) has been prepared from (I) by a known method; condensation with *p*-toluenesulphonamide gave a quantitative yield of 3-chloro-1-

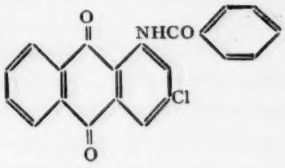
p-toluenesulphonamidoanthraquinone (III), hydrolysis of which with concentrated sulphuric acid gave (II), also in excellent yield. In combination



(II)



(III)

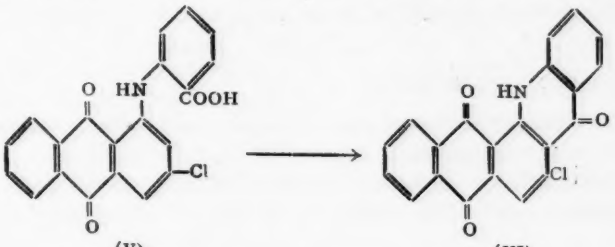


(IV)

with Naphtol AS, AS-LT and AS-D diazotized (II) produced bright red, red-brown and scarlet shades on cotton with light fastness 7-8, chlorine fastness 3-4, and soda boil fastness 2-3. For comparison diazotized 1-amino-4-chloroanthraquinone and 1-amino-2:4-dichloroanthraquinone were used for developing cotton yarn impregnated with Naphtol AS, when corinth and dull brown shades with light fastness 3-4, chlorine fastness 2-3 and soda boil fastness 1-2 were obtained.

1-Amino-3-chloroanthraquinone (II) was characterized by its N-acetyl and N-benzoyl (IV) derivatives. The latter (IV) dyed a brighter and deeper yellow than α-benzamidoanthraquinone. The chlorine atom in the 3-position also improved the light and soda boil fastness properties. The terephthaloyl and isophthaloyl derivatives of (II) were also prepared; these were found to give bright greenish yellow shades with improved chlorine and soda boil fastness when compared with Paradone Yellow 5GK and Indanthrene Yellow 5GK, the analogues from α-aminoanthraquinone. The light fastness, however, was inferior.

1-Anilino-3-chloroanthraquinone and its 2′-carboxy derivative (V) were prepared by condensing 1:3-dichloroanthraquinone (I) with aniline and anthranilic acid respectively. The anthranilic acid derivative (V) was cyclized to 7-chloroanthraquinoneacridone (VI) by means of phosphorus pentachloride in nitrobenzene. The acridone (VI) dyed a red-violet shade from a deep violet vat. It is of interest to note that (VI), which does not



(V) (VI)

have an amino group in the 6-position adjacent to the chlorine atom, was not dehalogenated by treatment with alkaline hydrosulphite at 30° for one hour.[7]

The chlorine atom in 1-amino-3-chloroanthraquinone (II) failed to react with *p*-toluenesulphonamide or anthranilic acid, but the N-benzoyl derivative condensed readily with *p*-toluenesulphonamide to give 1-benzamido-3-*p*-toluenesulphonamidoanthraquinone, which was hydrolysed with sulphuric acid to 1 : 3-diaminoanthraquinone.

EXPERIMENTAL

1 : 3-*Dichloroanthraquinone* (*I*)

A solution of 1-amino-2 : 4-dichloroanthraquinone (45 g.) in glacial acetic acid (450 c.c.) was cooled to 20° and poured into an ice-cold solution of sodium nitrite (45 g.) in conc. sulphuric acid (360 c.c.). After 30 minutes the mixture was diluted to 2 l. with ice-water, treated with 95% alcohol (1250 c.c.) and copper sulphate (10 g.), and refluxed for 3 hours. Dilution with water gave a product (40 g.) which was collected, and treated with chromic acid (5 g.) in boiling acetic acid (200 c.c.) for a few minutes. On filtering the hot solution and cooling, yellow needles of 1 : 3-dichloroanthraquinone, m.p. 208°, separated (Found: C, 60·3; H, 2·3; Cl, 25·8. Calc. for $C_{14}H_6Cl_2O_2$: C, 60·6; H, 2·4; Cl, 25·6%).

3-*Chloro*-1-p-*toluenesulphonamidoanthraquinone* (*III*)

A mixture of 1 : 3-dichloroanthraquinone (2 g.), *p*-toluenesulphonamide (1·8 g.), anhydrous sodium acetate (0·9 g.), copper acetate (0·1 g.) and amyl alcohol (25 c.c.) was refluxed for 15 hours. The product crystallized from glacial acetic acid in orange-red plates, m.p. 215° (Found: Cl, 8·5; N, 3·4. $C_{21}H_{14}ClNO_4S$ requires Cl, 8·6; N, 3·4%).

1-*Amino*-3-*chloroanthraquinone* (*II*)

3-Chloro-1-*p*-toluenesulphonamidoanthraquinone (0·5 g.) and conc. sulphuric acid (10 c.c.) were heated on a water-bath for 1 hour and poured into water. The product crystallized from acetic acid in red needles, m.p. 230° (Found: Cl, 13·6; N, 5·8. $C_{14}H_8ClNO_2$ requires Cl, 13·8; N, 5·5%).

1-*Acetamido*-3-*chloroanthraquinone*

1-Amino-3-chloroanthraquinone (0·5 g.) was boiled with acetic anhydride (1·8 c.c.) and sodium acetate (0·3 g.) for 3 hours. The yellow precipitate obtained on adding the solution to ice crystallized from alcohol in yellow plates, m.p. 216° (Found: N, 5·1. $C_{16}H_{10}ClNO_3$ requires N, 4·7%).

1-*Benzamido*-3-*chloroanthraquinone* (*IV*)

1-Amino-3-chloroanthraquinone (1·2 g.), benzoyl chloride (2 c.c.) and *o*-dichlorobenzene (10 c.c.) were heated at 190° for 2 hours, the solution cooled, and the precipitate collected. On recrystallization from *o*-dichlorobenzene yellow plates, m.p. 255°, were obtained (Found: Cl, 9·5; N, 3·9. $C_{21}H_{12}ClNO_3$ requires Cl, 9·8; N, 3·9%). The substance gives a red vat and dyes cotton a redder and deeper shade than α-benzamidoanthraquinone. The fastness properties are light 7, chlorine 4 and soda boil 4.

1-*Benzamido*-3-p-*toluenesulphonamidoanthraquinone*

A mixture of 1-benzamido-3-chloroanthraquinone (1·8 g.), *p*-toluenesulphonamide (1·0 g.), anhydrous potassium carbonate (0·5 g.), copper powder (0·1 g.) and nitrobenzene (100 c.c.) was refluxed for 6 hours. Nitrobenzene was removed by steam distillation, and the product filtered, washed and dried (2·1 g.). Crystallization from acetic acid gave yellow needles, m.p. 287–88° (Found: N, 5·7; S, 6·3. $C_{28}H_{20}O_5N_2S$ requires N, 5·7; S, 6·5%). The sulphonamide (0·5 g.) and concentrated sulphuric acid (15 c.c.) were heated on a water-bath for 8 hours, diluted with water and filtered. The red-brown product crystallized from *o*-dichlorobenzene in red rhomboidal plates, m.p. 290° (m.p. of 1 : 3-diaminoanthraquinone, 290°).[8]

Terephthalic acid derivative of 1-*amino*-3-*chloroanthraquinone*

Terephthalic acid (0·2 g.) was heated with thionyl chloride (5 c.c.) for 6 hours, excess thionyl chloride distilled off, and the residual acid chloride dried under vacuum on a water-bath for 2 hours. *o*-Dichlorobenzene (50 c.c.) and 1-amino-3-chloroanthraquinone (0·7 g.) were added and the solution refluxed for 2 hours, when yellow needles separated. After cooling, the product was collected (0·67 g.) and crystallized from nitrobenzene, when golden yellow needles, m.p. > 360°, were obtained (Found: N, 4·5. $C_{36}H_{20}Cl_2N_2O_6$ requires N, 4·4%). The substance dyes cotton a yellow shade from a violet vat (fastness to light 3, chlorine 4-5, and soda boil 4).

Isophthalic acid derivative of 1-*amino*-3-*chloroanthraquinone*

The chloride was prepared as above from isophthalic acid (0·5 g.) and heated with 1-amino-3-chloroanthraquinone (1·55 g.) and *o*-dichlorobenzene (50 c.c.) at the boil for 4 hours when a yellow product separated. On cooling, the dye was collected (1·5 g.) and crystallized from nitrobenzene. The yellow needles did not melt below 360° (Found: N, 4·3. $C_{36}H_{20}Cl_2N_2O_6$ requires N, 4·4%). The product dyes cotton a yellow shade from a violet vat (fastness to light 3, chlorine 4–5, soda boil 4).

Cotton dyed with the terephthalic and isophthalic acid derivatives of 1-amino-3-chloroanthraquinone was tendered by the action of light to a greater extent than cotton dyed with the aminoanthraquinone analogues. After exposure in a fadeometer for 48 hours, cotton dyed with the 1-amino-3-chloroanthraquinone derivatives gave cuprammonium fluidity values of 37·71 and 35·72 in comparison with the values of 31·83 for Paradone Yellow 5GK, 32·72 for Indanthrene Yellow 5GK, and 9·61 for the undyed cotton.

1-*Anilino*-3-*chloroanthraquinone*

1 : 3-Dichloroanthraquinone (2 g.), aniline (10 c.c.), anhydrous potassium acetate (0·6 g.) and a little copper acetate were refluxed for 1 hour and cooled. The mixture was poured into dilute hydrochloric acid and filtered. The precipitate (2·2 g.) crystallized from glacial acetic acid in long red-brown needles having a violet reflex. After two further crystallizations from the same solvent the m.p. was 166–67° (Found Cl, 10·9; N, 4·6. $C_{20}H_{22}ClNO_2$ requires Cl, 10·6; N, 4·2%). With concentrated sulphuric acid, a blue solution is obtained, which changes to violet on dilution and on further dilution gives a red-brown precipitate.

1-*Anthranilino*-3-*chloroanthraquinone* (*V*)

1 : 3-Dichloroanthraquinone (2·8 g.), anthranilic acid (2·1 g.), anhydrous potassium acetate (2·0 g.), copper bronze (50 mg.), copper acetate (50 mg.) and amyl alcohol (25 c.c.) were refluxed under stirring in an oil-bath at 155° for 3 hours. The mixture was filtered and the violet residue separated and boiled with hydrochloric acid. The product (3 g.) crystallized from toluene in brick-red needles, m.p. 272° (Found: Cl, 9·3; N, 3·7. $C_{21}H_{12}ClNO_4$ requires Cl, 9·5; N, 3·7%). The substance gives a yellow-brown solution in sulphuric acid and a red precipitate on dilution. With sodium hydroxide it gives a violet salt.

7-*Chloroanthraquinoneacridone* (*VI*)

1-Anthranilino-3-chloroanthraquinone (2 g.) was heated with toluene (20 c.c.) and phosphorus pentachloride (1·5 g.) for 30 minutes. The solution was cooled, the red product collected, washed with hexane, and a solution in nitrobenzene (12 c.c.) boiled till evolution of hydrochloric acid ceased. The product (1·7 g.) crystallized from *o*-dichlorobenzene in violet-red needles, m.p. 300° (Found: N, 3·8. $C_{21}H_{10}ClNO_3$ requires N, 3·9%). The acridone gives with sulphuric acid a yellow-orange solution and a red-violet precipitate on dilution. It dyes cotton a violet shade from a deep violet vat.

Summary

1 : 3-Dichloroanthraquinone has been prepared by the deamination of 1-amino-2 : 4-dichloroanthraquinone. The dichloroanthraquinone is useful for the preparation of 1-amino-3-chloroanthraquinone.

Acknowledgment

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NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XLVI. Synthesis in the Primetin Series

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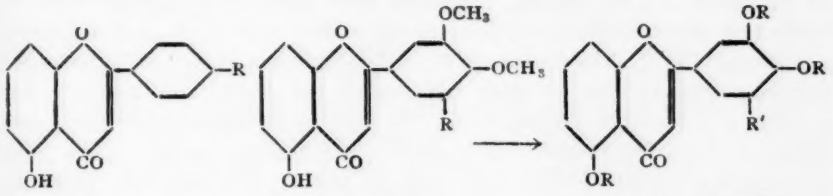
5-Hydroxy flavone (I *a*) occurs along with flavone in the deposits formed on the stalks and blossoms of *Primula imperialis*[1] and also probably in other species of *Primulæ*.[2] It was also synthesised by a number of workers starting from γ-resacetophenone (*see* Rajagopalan, Rao and Seshadri[3] for collected references). 5-Hydroxy-4′-methoxy flavone (I *b*) was prepared by Syed and Wheeler[4] and later by Baker, Flemons and Winter.[5]

The preparation of 5-hydroxy flavones with two and three hydroxyl (methoxyl) groups in the side-phenyl nucleus by Allan-Robinson method has now been investigated with the object of preparing the higher analogues of primetin by nuclear oxidation. The synthesis of 5-hydroxy-3′ : 4′ : 5′-trimethoxy flavone (II) from γ-resacetophenone by condensation with trimethylgallic anhydride and sodium trimethylgallate was examined under different conditions of hydrolysis. After the usual method of boiling with alcoholic potash for 20 minutes, it was noticed that the 3-acyl compound formed the major product which could later be deacylated to 5-hydroxy-3′ : 4′ : 5′-trimethoxy flavone by boiling with 10% sodium carbonate solution for 4 hours. In another experiment the product after condensation was directly boiled with 10% aqueous sodium carbonate for 4 hours and a fairly good yield of the free flavone was obtained. It was earlier observed by Baker, Flemons and Winter[5] during the preparation of 5-hydroxy-4′-methoxy flavone that refluxing the product with alcoholic alkali or sodium carbonate led to considerable loss; consequently they adopted a different method for working up the condensation product. It was shaken with ethyl acetate and cold 10% sodium carbonate solution for 18 hours when a good yield of 5-hydroxy-4′-methoxy-3-anisoyl flavone was obtained. But during the next stage when deacylation was attempted with sodium carbonate or sodium hydroxide considerable destruction of the flavone was encountered. In the

present work, the crude product was shaken with ether and 10% sodium carbonate for 24 hours. A mixture of the 3-acyl compound and the free flavone was frequently obtained and their proportions varied considerably in different experiments. They could, however, be separated by taking advantage of the greater solubility of the 3-acyl flavone in a mixture of alcohol and acetone. The yield of the 5-hydroxy-3′ : 4′ : 5′-trimethoxy flavone during these different experiments varied very much and the yields were not consistent.

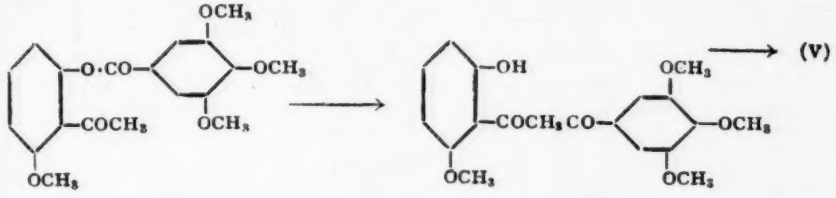


I *a*, R=H
I *b*, R=OCH_3

II, R=OCH_3
VI, R=H

V, R=CH_3, R′=OCH_3
VII, R=CH_3, R′=H
VIII, R=R′=H
IX, R=H; R′=OH

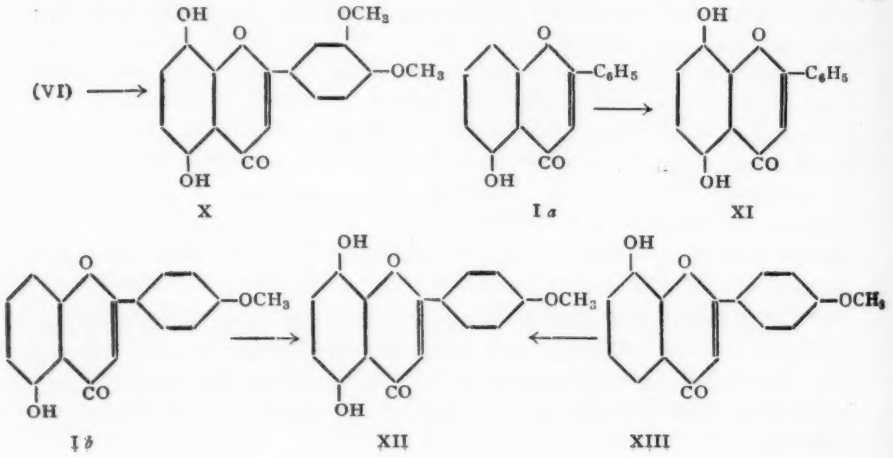
An alternative method was also tried for the preparation of the same flavone. 2-Hydroxy-6-methoxy acetophenone was condensed with trimethylgalloyl chloride in the presence of anhydrous pyridine. Attempts to convert the resulting ester (III) into the dibenzoyl methane (IV) by the use of sodamide in toluene solution were unsuccessful; but success was achieved by the use of powdered potassium hydroxide in dry pyridine.[6] The diketone could be converted into the 5 : 3′ : 4′ : 5′-tetramethoxy flavone (V) by refluxing with fused sodium acetate in glacial acetic acid solution though the yields were not very satisfactory.



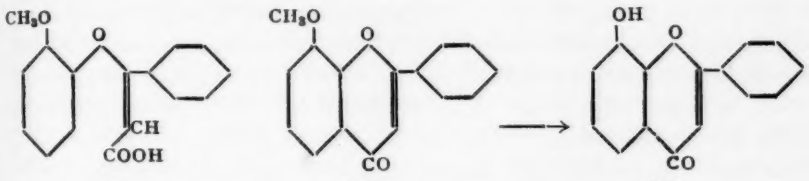
III IV

5-Hydroxy-3′ : 4′-dimethoxy flavone (VI) was also prepared by the Allan-Robinson method. The dimethoxy and the trimethoxy-5-hydroxy flavones were methylated and demethylated by the usual methods and the corresponding methyl ethers (VII and V) and the hydroxy compounds (VIII) and (IX) obtained.

In an attempt to prepare the analogues of primetin, 5-hydroxy-3′: 4′-dimethoxy (VI) and 5-hydroxy-3′: 4′: 5′-trimethoxy (II) flavones have been subjected to oxidation with alkaline persulphate. Owing to the sparing solubility of these compounds in alkali, pyridine is employed to keep them in solution. The yield of the oxidation product (X) is very poor in the case of (VI) while (II) does not undergo any oxidation at all. It may be noted in this connection that 5-hydroxy flavone (I *a*) itself gives fairly good yields of primetin (XI) by nuclear oxidation with alkaline persulphate[3] and 5-hydroxy-4′-methoxy flavone (I *b*) gives about 20% yield of the 5: 8-dihydroxy compound[5] (XII). The reason for the difficulty in the oxidation of the higher members may be that in these compounds the 5-hydroxyl group is not activating adequately the 8-position. It may be mentioned that these substances are sparingly soluble in aqueous alkali because of the chelate bond between the 5-hydroxyl and the carbonyl groups. Though they could be brought into solution by means of pyridine, adequate quantity of the oxide ion is probably not formed and consequently activation of the 8-position is not enough. In the alternative method of preparing members of the primetin series, 8-hydroxy flavones can be used for this nuclear oxidation. Since they are more easily soluble in alkali they could form the oxide ions better and hence the 5-position could be adequately oxidised. Hence it was considered to be of special interest to study the persulphate oxidation of 8-hydroxy flavone derivatives. One such example 8-hydroxy-4′-methoxy flavone (XIII) was investigated by Baker *et al.*[5] and they reported that the yield was poor, about 3%.



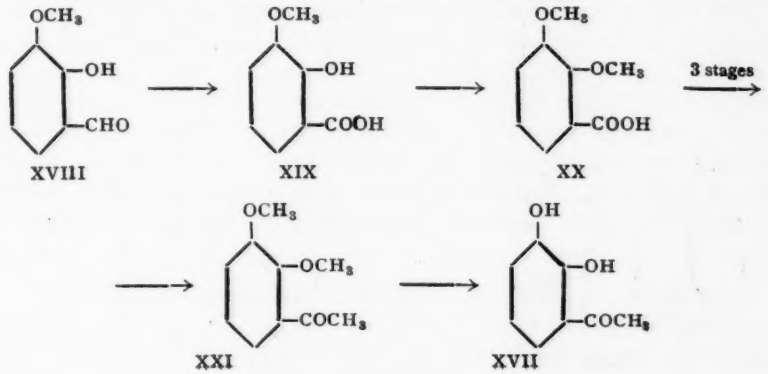
8-Hydroxy flavone (XIV) was first prepared by Ruhemann[7] by cyclisation of β-guiaicoxy cinnamic acid (XV) and subsequent demethylation of the intermediate 8-methoxy flavone (XVI).



XV XVI XIV

8-Hydroxy-4′-methoxy flavone (XIII) was prepared by Baker, Flemons and Winter[5] from 2 : 3-dihydroxy acetophenone (XVII) employing the Allan-Robinson condensation. The required ketone was obtained by Baker and Smith[8] from 2 : 3-dimethoxybenzonitrile which was treated with methyl-magnesium iodide and the resulting product decomposed with dilute acetic acid; the dimethoxy acetophenone thus prepared was demethylated by boiling with hydrobromic acid in glacial acetic acid solution. It was also earlier obtained by oxidation of 2 : 3-dimethoxyphenylmethyl carbinol with chromic acid.[9]

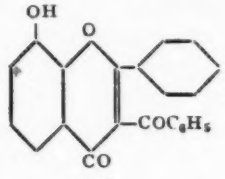
In the present investigation the required ketone (XVII) was obtained from orthovanillin (XVIII) by using the following steps. It was first oxidised to orthovanillic acid (XIX) by fusion with potash[10] and the resulting acid methylated to orthoveratric acid (XX). Its chloride was condensed with acetoacetic ester and sodium alcoholate in dry ether medium. The product formed (2 : 3-dimethoxybenzoyl acetoacetic ester) was directly hydrolysed by refluxing with 33% sulphuric acid for 10 hours. The resulting dimethoxy acetophenone (XXI) was characterised by its boiling point (143–44° at14 mm.).



XVIII XIX XX XXI XVII

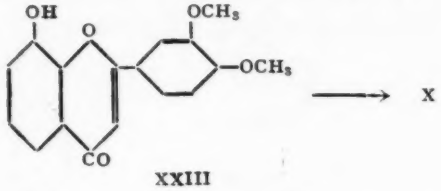
and the preparation of the oxime. The 2: 3-dimethoxy acetophenone was demethylated to 2: 3-dihydroxy acetophenone (XVII) by refluxing with aqueous hydrobromic acid (48%) and glacial acetic acid for 5 hours.[8]

8-Hydroxy flavone (XIV) was now prepared by condensing 2: 3-dihydroxy acetophenone (XVII) with benzoic anhydride and sodium benzoate by the Allan-Robinson method. Hydrolysis was effected by refluxing the reaction product with alcoholic potash (8%) for 20 minutes. The 3-acyl compound (XXII) was deacylated by refluxing with sodium carbonate solution (5%) for 2 hours. 5: 8-Dihydroxy flavone (XI) (primetin) was obtained by the persulphate oxidation of 8-hydroxy flavone and the yield was about (15%).

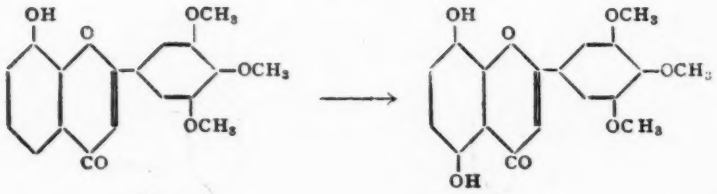


XXII

8-Hydroxy-3′: 4′-dimethoxy (XXIII) and 8-hydroxy-3′: 4′: 5′-trimethoxy flavones (XXIV) were obtained by condensing 2: 3-dihydroxy acetophenone (XVII) with the anhydride and sodium salt of veratric acid and of trimethyl gallic acid respectively. The flavones were oxidised by alkaline persulphate to 5: 8-dihydroxy-3′: 4′-dimethoxy flavone (X) and 5: 8-dihydroxy-3′: 4′: 5′-trimethoxy flavone (XXV) respectively (10% yields). (XXIII) and (XXIV) have been methylated and demethylated by the usual methods and the corresponding methyl ethers and the hydroxy compounds obtained.



XXIII



XXIV XXV

Experimental

5-Hydroxy-3′ : 4′ : 5′-trimethoxy flavone (II)

An intimate mixture of γ-resacetophenone (3 g.), trimethylgallic anhydride (24 g.) and sodium trimethylgallate (6 g.) was heated under reduced pressure at 180° C. for 4 to 5 hours. The product was then worked up using different conditions for hydrolysis:—

Method (1).—The hydrolysis was carried out by refluxing for 20 minutes with aqueous alcoholic potassium hydroxide (8 g. in 150 c.c.). The alcohol was removed under reduced pressure, the residue taken up in water and carbon dioxide passed through the suspension for 4 hours. The precipitated solid was found to be largely the 3-acyl derivative. It was purified by recrystallisation from alcohol when the 5-hydroxy-3′ : 4′ : 5′-trimethoxy-3-trimethylgalloyl flavone was obtained as pale yellow long thin plates melting at 147–48° C. Yield, 1·5 g. (Found: C, 64·3; H, 5·0. $C_{28}H_{26}O_{10}$ requires C, 64·4; H, 5·1%). The 3-acyl group was removed by boiling this compound with 10% aqueous alcoholic sodium carbonate solution for 4 hours. The free flavone was crystallised from a large volume of alcohol when it was obtained as bright yellow thick rods melting at 194–95°. (Found: C, 66·1; H, 5·0; $C_{18}H_{16}O_6$ requires C, 65·8 and H, 4·9%.)

The substance is insoluble in cold aqueous sodium hydroxide; on boiling it is converted into the bright yellow, sparingly soluble sodium salt. It dissolves to a pale yellow solution in concentrated sulphuric acid which shows no fluorescence but slowly turns brown. The compound gives a pink brown colour with alcoholic ferric chloride which becomes dark brown with excess.

Method (2).—The crude condensation product was broken up, suspended in alcohol (50 c.c.) and refluxed with 10% sodium carbonate solution (100 c.c.) for a period of 4 hours. The mixture which consisted of a suspension of the sparingly soluble, bright yellow sodium salt was acidified with dilute hydrochloric acid and the mixture of flavone and trimethylgallic acid which separated was filtered. It was stirred into an excess of aqueous sodium bicarbonate solution, the undissolved flavone filtered, washed well with water and then crystallised from a large volume of alcohol. 5-Hydroxy-3′ : 4′ : 5′-trimethoxy flavone was obtained as bright yellow thick rods melting at 194-95° C. Yield, 1·1 g.

Method (3).—The product from the Allan-Robinson condensation was broken up and treated with aqueous sodium carbonate (10%, 200 c.c.) and ether (100 c.c.) and the mixture shaken occasionally in the cold for 24 hours.

The ether layer was separated, washed successively with sodium bicarbonate solution and then with water. The solid which was left behind after removal of the solvent was crystallised from alcohol. The composition of the product varied in different experiments and consisted sometimes of the 3-acyl compound and at other times of the free flavone as the major fraction.

5 : 3′ : 4′ : 5′-*Tetramethoxy flavone* (*V*)

5-Hydroxy-3′ : 4′ : 5′-trimethoxy flavone (0·8 g.) was dissolved in 50 c.c. of dry acetone and redistilled dimethyl sulphate (1 c.c.) and freshly ignited potassium carbonate (3 g.) were added. The mixture was gently refluxed on a water-bath and after 15 hours another lot of 0·5 c.c. of dimethyl sulphate was added. The refluxing was continued for a total period of 32 hours after which time the acetone solution was filtered, the inorganic salts washed with warm acetone and the solvent distilled off. An yellowish oil was obtained which quickly solidified on rubbing with a glass rod. It was filtered, washed with water and crystallised twice from dilute alcohol (charcoal) when the tetramethoxy flavone was obtained as long colourless needles melting at 148–49° after drying. (Found: C, 66·8; H, 4·7. $C_{19}H_{18}O_6$ requires C, 66·6 and H, 5·2%.)

5 : 3′ : 4′ : 5′-*Tetrahydroxy flavone* (*IX*)

The trimethoxy flavone (1 g.) was dissolved in acetic anhydride (10 c.c.) by warming and to the solution was added hydriodic acid (15 c.c.; d. 1·7) in small quantities with cooling. The mixture was refluxed in an oil-bath for 2½ hours, cooled and treated with an excess of a saturated solution of sodium bisulphite. The brown solid which separated was filtered and repeatedly extracted with hot acetone, the acetone solution filtered and concentrated when an yellow solid was obtained. When crystallised twice from acetone-alcohol mixture it came out as clusters of yellow prisms turning brown at 290° and decomposing at 310–12° C. Yield, 0·6 g. (Found: C, 62·7, H, 4·0. $C_{15}H_{10}O_6$ requires C, 62·9 and H, 3·5%). The tetra-acetate prepared as usual melted at 225–26°.

2-*Trimethylgalloyloxy*-6-*methoxy acetophenone* (*III*)

Dry trimethylgallic acid (2 g.) was treated with thionyl chloride (3 c.c.) and the mixture heated on a water-bath for half an hour. The excess of thionyl chloride was then distilled away and monomethyl ether of γ-resacetophenone (0·5 g.) added followed by 6 c.c. of anhydrous pyridine. The mixture was heated on a water-bath for 1 hour and then treated with ice-cold dilute hydrochloric acid. The precipitated solid was extracted with ether and the ethereal solution was successively washed with dilute sodium

hydroxide, dilute hydrochloric acid and water. The ester obtained after removal of the solvent crystallised from alcohol as colourless long thin plates melting at 153–54° C. Yield, 0·5 g. (Found: C, 63·1; H, 5·8. $C_{19}H_{20}O_7$ requires C, 63·3 and H, 5·5%).

2-Hydroxy-6 : 3′ : 4′ : 5′-tetramethoxy dibenzoyl methane (IV)

The above ester (1 g.) was dissolved by warming in 10 c.c. of dry pyridine, then treated with finely powdered potassium hydroxide (1·2 g.) and shaken vigorously. The temperature was maintained at 40° by occasional warming in a water-bath. The solution soon became deep yellow and thick due to the separation of the potassium salt of the diketone. After 15 minutes the mixture was acidified with 100 c.c. of cold 20% acetic acid when a yellow semi-solid separated which soon solidified. It was filtered, washed thoroughly with water and crystallised from benzene-petroleum ether mixture. The diketone was obtained as bright yellow broad prisms and plates melting at 150–51° C. Yield, 0·6 g. (Found: C, 63·5, H, 5·6. $C_{19}H_{20}O_7$ requires C, 63·3 and H, 5·5%.) It gave a pink-brown colour with ferric chloride in alcoholic solution, and turned reddish-brown with excess.

5 : 3′ : 4′ : 5′-Tetramethoxy flavone

The diketone (1 g.) was dissolved in frozen and remolten acetic acid (20 c.c.) and fused sodium acetate (3 g.) added and the mixture refluxed for 2 hours. It was then diluted with water, the precipitated solid filtered and recrystallised from dilute alcohol. It melted at 147° and did not depress the melting point of the tetramethoxy flavone prepared earlier. Yield, 0·3 g.

5-Hydroxy-3′ : 4′-dimethoxy flavone (VI)

An intimate mixture of γ-resacetophenone (3 g.), veratric anhydride (24 g.) and sodium veratrate (6 g.) was heated under reduced pressure at 180° for 5 hours. The product was broken up and treated with 10% aqueous sodium carbonate solution (200 c.c.) and ether (100 c.c.) and the mixture occasionally shaken in the cold for 24 hours. The ether layer was worked up as before, and the pale yellow solid was crystallised from alcohol when the 5-hydroxy-3′ : 4′ -dimethoxy-3-veratroyl flavone was obtained as yellow prisms melting at 142–43°. Yield, 1·0 g. (Found: C, 67·7, H, 5·0. $C_{26}H_{22}O_8$ requires C, 67·5 and H, 4·8%.) In a number of experiments, the amount of the free flavone isolated by this method was found to be very little.

The hydrolysis of the 3-acyl group was carried out by boiling with 10% aqueous-alcoholic sodium carbonate and the flavone isolated in the usual manner. It crystallised from alcohol as pale yellow plates and prisms melting

at 165-66°. (Found: C, 68·0, H, 4·8. $C_{17}H_{14}O_5$ requires C, 68·4 and H, 4·7%.) The compound dissolves with difficulty in 5% sodium hydroxide to give an yellow solution from which the yellow sodium salt slowly separates. It gives a pink brown colour with alcoholic ferric chloride and turns purple-brown with excess.

5 : 3′ : 4′-*Trimethoxy flavone* (*VII*)

The dimethoxy flavone (0·25 g.) was methylated by refluxing in anhydrous acetone (50 c.c.) solution with redistilled dimethyl sulphate (2 c.c.) and ignited potassium carbonate (5 g.) for 40 hours. The trimethyl ether crystallised from dilute alcohol as long, colourless needles and thin rods and melted at 139–40° after drying at 100° for 4 hours. The compound dissolves in concentrated sulphuric acid to a bright yellow solution showing no fluorescence. The solution slowly turns brown and then green in 24 hours.

5 : 3′ : 4′-*Trihydroxy flavone* (*VIII*)

The dimethoxy flavone (2 g.) was demethylated in acetic anhydride (15 c.c.) solution by boiling with hydriodic acid (d. 1·7, 20 c.c.) for 4 hours. The brown solid product was recrystallised from methyl alcohol and the trihydroxy flavone obtained as pale yellow plates darkening at 260° and decomposing at 278–80° C. Yield 0·8 g. In 5% sodium hydroxide the substance dissolves immediately to a deep yellow solution which quickly turns brown on shaking. With ferric chloride it gives a brown colour in alcoholic solution.

5 : 8-*Dihydroxy*-3′ : 4′-*dimethoxy flavone* (*X*).—A solution of potassium persulphate (1·2 g. in 100 c.c.) was added dropwise to a mechanically stirred solution of 5-hydroxy-3′ : 4′-dimethoxy flavone (0·8 g.) in a mixture of aqueous potash (2 g. in 25 c.c.) and pyridine (25 c.c.) during 2 hours. The stirring was continued for another 4 hours after which the contents were left for 36 hours. After acidification with hydrochloric acid a small quantity of unchanged flavone was extracted with ether (25 c.c.; thrice); a further amount of concentrated hydrochloric acid (15 c.c.) was added and the mixture kept on a boiling water-bath for 20 minutes. It was then repeatedly extracted with ether and the quinol obtained by removal of the solvent. The yellow solid crystallised from ethyl acetate as bright yellow small plates sintering at 235° and melting with decomposition at 240° C. A mixed melting point determination with a sample prepared by the oxidation of 8-hydroxy-3′ : 4′-dimethoxyflavone showed no depression. Yield, 80 mg.

In aqueous sodium carbonate the quinol dissolves instantly to a red solution which rapidly changes to green and fades off to yellow. In aqueous

sodium hydroxide it gives a greenish solution quickly turning pale pink and fading to brownish-yellow. The compound gives a brown ferric reaction, after the production of an initial green colour.

2: 3-*Dimethoxybenzoyl acetoacetic ester*

Separate solutions of sodium (2·49 g., 0·3 mole) in absolute alcohol (42 c.c.) and of 2: 3-dimethoxybenzoyl chloride (10 g., 0·15 mole) in absolute ether (210 c.c.) were prepared. Half of the sodium alcoholate solution (21 c.c.) was mixed with acetoacetic ester (7·01 g., 0·15 mole) and to this half of the ethereal solution of dimethoxybenzoic acid chloride (105 c.c.) was added and the mixture shaken in the cold for half an hour. A mixture of sodium chloride and the sodium salt of the dimethoxybenzoyl acetoacetic ester gradually separated. After half an hour, sodium alcoholate solution (10·05 c.c.) and dimethoxybenzoyl chloride solution (50 c.c.) were added and the shaking continued for another half an hour. The condensation was completed by the addition of the remaining sodium alcoholate solution (10·05 c.c.) and the acid chloride solution (50 c.c.). The reaction flask was then kept overnight in the refrigerator. The salts which separated were filtered, washed with absolute ether and directly put up for hydrolysis with dilute sulphuric acid.

2: 3-*Dimethoxy acetophenone* (*XXI*)

The sodium salt of 2: 3-dimethoxybenzoyl acetoacetic ester obtained above was refluxed with excess of 33% sulphuric acid (200 c.c.) for 8 hours. The solution along with the oily material was then cooled and extracted with ether. The ethereal solution was thoroughly washed with 5% alkali to remove any free acid present, then with water and dried over anhydrous sodium sulphate. The solvent was removed and the 2: 3-dimethoxy acetophenone distilled under reduced pressure (143–44° at 14 mm.). Yield, 4 g.

The oxime was prepared by refluxing a solution of 2: 3-dimethoxy acetophenone (2·5 g.) in 10 c.c. alcohol with hydroxylamine hydrochloride (3 g. in 5 c.c. water) and sodium acetate (5·1 g.) for 2 hours. After crystallisation from alcohol it melted at 96–97°.

2: 3-*Dihydroxy acetophenone* (*XVII*)

2: 3-Dimethoxy acetophenone (1 g.) was demethylated by refluxing with hydrobromic acid (8 c.c., d. 1·5) in acetic acid solution (8 c.c.) for 5 hours according to the method of Baker and Smith.[8] On crystallisation from dilute methanol the dihydroxy acetophenone came out as pale yellow plates melting at 97–98° C. Yield, 0·6 g. It gave a green colour with alcoholic ferric chloride solution.

8-Hydroxy flavone (XIV)

An intimate mixture of 2:3-dihydroxy acetophenone (3·5 g.), benzoic anhydride (30 g.) and sodium benzoate (8 g.) was heated under reduced pressure at 180–85° for 10 hours. The cake was then broken up, stirred with alcohol (150 c.c.) and refluxed with potassium hydroxide solution (15 g. in 15 c.c. water) for 20 minutes. The alcohol was removed under reduced pressure, the residue dissolved in water (300 c.c.) and the alkaline solution extracted with ether to remove oily impurities. Carbon dioxide was then passed into the solution for 4 hours, the brown mass that separated was filtered and extracted with benzene (8–10 times; 100 c.c. each time). The benzene solution on concentration gave the 3-acyl flavone (XXII). A further quantity was obtained by extracting the mother liquor with benzene. It crystallised from benzene as colourless, thick prisms melting at 223–24° C. Yield, 3·5 g.

The 3-acyl group was removed by refluxing the substance with sodium carbonate solution (100 c.c.; 5%) for 2 hours. The solution was then acidified with hydrochloric acid in the hot and the solid filtered. It was washed with a small quantity of hot water and crystallised from alcohol when the 8-hydroxy flavone was obtained as colourless, stout rods melting at 249–50° C. Ruhemann records the melting point of 8-hydroxy flavone as 250°. Yield, 1·7 g. It dissolved in 5% sodium hydroxide to a brown solution and gave a light brown colour with alcoholic ferric chloride.

8-Acetoxy flavone was prepared by heating 8-hydroxy flavone with acetic anhydride and 2 drops of dry pyridine at 140-50° for 2 hours. The acetate crystallised from a mixture of benzene and petrol as bunches of colourless needles melting at 142-43° C. 8-Methoxy flavone prepared by methylation of 8-hydroxy flavone in acetone solution with methyl sulphate and potassium carbonate crystallised from dilute alcohol as bunches of colourless, long needles and melted at 199–200°.

5:8-Dihydroxy flavone: Primetin (XI)

8-Hydroxy flavone (1·5 g.) was dissolved in sodium hydroxide solution (2·25 g. in 50 c.c. water) and the yellowish-brown solution continuously stirred with a magnetic stirrer. A solution of sodium persulphate (1·5 g. in 40 c.c. water) was then added dropwise during the course of 2 hours, the temperature of the contents being maintained at 15-20° C. throughout the experiment. After the addition was complete, the strirring was continued for another hour and the solution left overnight. It was then acidified to congo red with hydrochloric acid when some of the original product separated. This was filtered and the filtrate extracted with ether. Sodium

bisulphite (0·2 g.) and concentrated hydrochloric acid (25 c.c.) were added and the solution heated on a water-bath at 75–80° for 15 minutes. After cooling it was extracted with ether, the solvent distilled and the brown powder dried and crystallised from a mixture of ethyl acetate and petrol. The product separated as bright yellow plates melting at 227–29° C. Yield, 0·2 g. It gave a green colour with alcoholic ferric chloride solution and agreed in all its properties with primetin.[3] Mixed melting point with an authentic sample was undepressed.

8-*Hydroxy*-3′ : 4′-*dimethoxy flavone* (*XXIII*).—

2 : 3-Dihydroxy acetophenone (5·6 g.), veratric anhydride (50 g.) and sodium salt of veratric acid (10 g.) were thoroughly mixed and heated at 180–85° under diminished pressure for 12 hours. The product was worked up as before and the 3-veratroyl flavone crystallised from a mixture of benzene and ethyl acetate when it separated as colourless, small prisms melting at 134–35° C. Yield, 5·0 g. (Found: C, 67·6; H, 4·9. $C_{26}H_{22}O_8$ requires C, 67·5 and H, 4·7%.) It gave a light brown colour with alcoholic ferric chloride.

Deacylation of the 3-acyl compound was effected by refluxing it with sodium carbonate solution (5%, 150 c.c.) for 2 hours, and the 8-hydroxy-3′ : 4′-dimethoxy flavone was crystallised from a mixture of methyl alcohol and ethyl acetate. It came out as pale brown, short needles melting at 254–55° C. Yield, 2·1 g. (Found: C, 66·7; H, 4·8. $C_{17}H_{14}O_5$, $\frac{1}{2}H_2O$ requires C, 66·4 and H, 4·8%.) It gave a light brown colour with alcoholic ferric chloride solution. An alcoholic solution of the flavone developed an orange colour on reduction with magnesium and hydrochloric acid.

The acetate was prepared by heating with acetic anhydride and a drop of dry pyridine. It crystallised from ethyl alcohol as yellow long thin rods melting at 174–75° C. (Found: C, 67·7; H, 5·2. $C_{19}H_{16}O_6$ requires C, 67·1 and H, 4·7%).

8 : 3′ : 4′-*Trimethoxy flavone*

8-Hydroxy-3′ : 4′-dimethoxy flavone was methylated by refluxing with excess of dimethyl sulphate and anhydrous potassium carbonate in dry acetone solution for 8 hours. The methyl ether crystallised from methyl alcohol as yellow small rectangular prisms melting at 148–49° C.

8 : 3′ : 4′-*Trihydroxy flavone*

To a suspension of 8-hydroxy-3′ : 4′-dimethoxy flavone (0·2 g.) in acetic anhydride (5 c.c.) was added hydriodic acid (5 c.c.; d. 1·7) cautiously

with cooling in ice. The solution was refluxed (147–50°) for 2 hours, diluted with ice-cold water and treated with a saturated solution of sodium bisulphite (20 c.c.). The contents were cooled and the solid that separated was filtered and dried. The trihydroxy flavone crystallised from a mixture of ethyl acetate and acetone (charcoal) as very pale yellow, tiny prisms melting at 275–76° C. Yield, 0·15 g. An alcoholic solution of the compound gave a grass green colour with ferric chloride. (Found: C, 66·2; H, 3·9. $C_{15}H_{10}O_6$ requires C, 66·6 and H, 3·7%).

The triacetate prepared by the usual method was crystallised from a mixture of ethyl acetate and methyl alcohol and was obtained as colourless, long woolly needles, melting at 213–14° C. (Found: C, 63·6; H, 4·0; $C_{21}H_{16}O_8$ requires C, 63·7 and H, 4·1%).

5 : 8-*Dihydroxy*-3′ : 4′-*dimethoxy flavone* (*X*)

8-Hydroxy-3′ : 4′-dimethoxy flavone (1·5 g.) was dissolved in sodium hydroxide solution (1 g. in 50 c.c. water) and to the light-brown solution was added dropwise a solution of sodium persulphate (2·3 g. in 30 c.c. water) during the course of 2½ hours. Throughout the addition the mixture was kept mechanically stirred and the temperature maintained at 15–20°. Stirring was then continued for another hour and the contents left overnight at room temperature. After working up as before the oxidation product was obtained as a brown powder. It was dried and crystallised from a mixture of ethyl acetate and petrol when 5 : 8-dihydroxy-3′ : 4′-dimethoxy flavone separated as small yellow broken plates. It sinters at 230°, melts at 234–35° and decomposes at 240° C. Yield, 0·15 g. Mixed melting-point with a sample prepared by the persulphate oxidation of 5-hydroxy-3′ : 4′-dimethoxy flavone was undepressed. With ferric chloride an alcoholic solution of the compound gave a green colour which changed to brown after some time. (Found: C, 61·7; H, 4·6. $C_{17}H_{14}O_6$, H_2O requires C, 61·4 and H, 4·8%.)

8-*Hydroxy*-3′ : 4′ : 5′-*trimethoxy flavone* (*XXIV*)

An intimate mixture of 2 : 3-dihydroxy acetophenone (3·5 g.), trimethylgallic anhydride (32 g.) and sodium salt of trimethylgallic acid (8 g.) was heated under reduced pressure at 180–85° for 10 hours. The product was worked up as before and was found to consist of only the free flavone with practically no admixture of the 3-acyl compound. On crystallisation from a mixture of ethyl acetate and acetone (charcoal) it separated as pale yellow, short needles melting at 228–30° C. Yield, 1·3 g. It does not give any distinct colour with alcoholic ferric chloride. (Found: C, 65·9; H, 5·3. $C_{18}H_{16}O_6$ requires C, 65·8 and H, 4·9%.)

The acetate crystallised from ethyl acetate as colourless, woolly needles melting at 194–95° C.

8 : 3′ : 4′ : 5′-*Tetramethoxy flavone*

8-Hydroxy-3′ : 4′ : 5′-trimethoxy flavone was methylated in dry acetone solution by refluxing with excess of dimethyl sulphate and anhydrous potassium carbonate for 8 hours. The methyl ether crystallised from methyl alcohol as pale yellow long thin plates melting at 189–90° C. (Found: C, 64·9; H, 5·0; $C_{19}H_{18}O_6$, $\frac{1}{2}H_2O$ requires C, 64·9; H, 5·4%).

8 : 3′ : 4′ : 5′-*Tetrahydroxy flavone*

The demethylation of 8-hydroxy-3′ : 4′ : 5′-trimethoxy flavone (0·15 g.) was carried out by boiling in acetic anhydride (5 c.c.) solution with hydriodic acid (5 c.c., d. 1·7) for 2 hours. The tetrahydroxy flavone crystallised from a mixture of ethyl acetate and methyl alcohol (charcoal) as colourless short prismatic needles melting at 320–22° C. Yield, 0·1 g. It gave a green colour with alcoholic ferric chloride.

The tetra-acetate was prepared by heating with acetic anhydride and a drop of dry pyridine for 2 hours. It crystallised from ethyl acetate as colourless flat needles and plates melting at 200–1° C.

5 : 8-*Dihydroxy*-3′ : 4′ : 5′-*trimethoxy flavone* (*XXV*)

8-Hydroxy-3′ : 4′ : 5′-trimethoxy flavone (1 g.) was dissolved in sodium hydroxide solution (0·5 g. in 15 c.c. water) and the oxidation was carried out with sodium persulphate solution (1·5 g. in 35 c.c. water) as in the previous case. The quinol was crystallised from a mixture of ethyl acetate and acetone (charcoal) when it separated as aggregates of yellow plates. It shrinks at 250° and melts at 255° C. Yield, 0·1 g.. The compound gave a green colour with alcoholic ferric chloride solution. (Found: C, 63·0; H, 5·0. $C_{18}H_{16}O_7$ requires C, 62·8 and H, 4·7%.)

Summary

The two higher analogues of 5-hydroxy flavone (primuletin) containing two and three methoxyl groups in the side phenyl nucleus have been synthesised and subjected to persulphate oxidation. 5-Hydroxy-3′ : 4′-dimethoxy flavone gave poor yield of dimethoxy primetin while the higher member could not be oxidised under these conditions. Alternatively, oxidation of 8-hydroxy flavones has been attempted and found to proceed more satisfactorily to yield primetin and its higher members. The required 8-hydroxy flavones

have been made from 2: 3-dihydroxy acetophenone for the preparation of which a convenient method has been worked out starting from ortho vanillin.

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MEASUREMENT OF ULTRASONIC VELOCITIES IN SOME INDIAN ROCKS

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I. Introduction

The determination of elastic constants of solids, by the ultrasonic wedge method has engaged the attention of Bhagavantam (1944, 1945) and his co-workers in this laboratory for several years. In extending such studies, a different technique, based on a principle originally used by Bez-Bardili (1935), has now been developed by us. Sound velocities in solids are usually much higher than in liquids, so that when an ultrasonic beam passes from a liquid to a solid, the phenomenon of total internal reflection will occur beyond a critical angle of incidence, as in optics. If this critical angle is determined, the ultrasonic velocity in one medium with respect to that in the other can be calculated. In the method of Bez-Bardili a plate of the material is placed in the path of the ultrasonic beam in a liquid and rotated. The emergent beam is detected by the Debye-Sears diffraction method. More recently Schneider and Burton (1949) employed a second piezoelectric crystal to detect the transmitted beam. In our investigation, the pulse technique of Pellam and Galt (1946) is adapted to work on this principle. Others who worked on these lines are Srivastava (1949) and Krishnaji (1950).

This paper gives the elastic constants, based on the measurement of longitudinal as well as torsional velocities, for a number of Indian rocks, for the first time. Longitudinal velocities in some Indian rocks were determined by Prasada Rao (1946) using the wedge method and one of the present authors (1952) extended this method to determine longitudinal and torsional velocities in certain cases. It was, however, not possible to excite torsional modes in cases like Granite, Dolerite, etc., by using the wedge method. A particular advantage of the pulse method now developed is the ease and accuracy with which torsional velocities can be determined even in such rocks.

2. Experimental Arrangement

A pulsed ultrasonic beam is generated by oscillating one crystal and received by another identical crystal as shown in Fig. 1, the intervening

space being filled with a liquid. The two crystals are ground flat to the same thickness, their fundamental frequency being 1·15 MC/S and the third harmonic is used throughout this investigation. The liquid comes into contact with the crystals through a circular aperture of about 1 cm. diameter in the crystal holder. To prevent the ultrasonic beam from becoming divergent, a long narrow tube is interposed in front of the transmitting crystal, which restricts the beam to a narrow parallel pencil of rays.

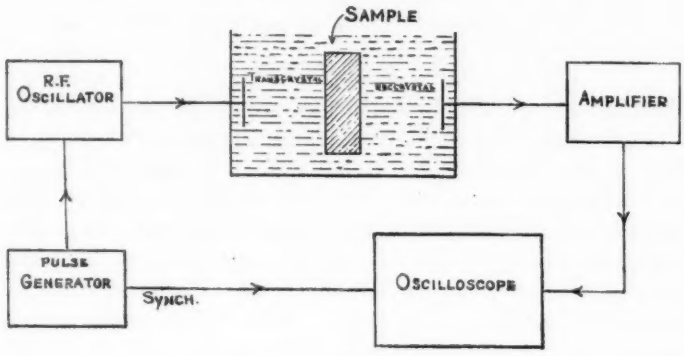

FIG. 1

The material under investigation is in the form of a rectangular plate and is mounted on a vertical axis of rotation which is also the axis of a slow motion drive having a graduated screw with a least count of 0·072°. The plate so mounted is interposed in the path of the ultrasonic beam and rotated, thereby changing the angle of incidence of the beam on the plate. The intensity of the transmitted pulse, as indicated by the pattern on the oscilloscope, changes with variation in the angle of incidence.

The incident ultrasonic beam is split into two components inside the plate, corresponding to the longitudinal and torsional modes of propagation. In most solids both these waves travel with a much higher velocity than in the liquid medium. Hence both components are refracted away from the normal, the angle of refraction following the well-known sine law. For each of these two components, there is a limiting angle of incidence at which total reflection of that component occurs. These critical angles are given by

$$\text{Sin } i_L = V_l/V_L; \quad \text{Sin } i_T = V_l/V_T \qquad (1)$$

where V_l, V_L and V_T are velocities in the liquid and of the longitudinal and torsional modes in the solid respectively. As the torsional velocity is always

less than the longitudinal velocity, the transmitted beam first exhibits a sharp dip in intensity at the longitudinal critical angle and completely vanishes a little later at the torsional critical angle.

It is important to mention here that the emergent beam is shifted laterally with respect to the incident beam due to refraction, so that the receiving crystal should either cover a large area or be capable of being moved laterally to pick up the transmitted beam. For the same reason, it is necessary to have a plate of as large dimensions as possible.

It has been observed by previous workers that the ultrasonic velocities as measured by this method show a marked dependence on the thickness of the plate used. An empirical relation was proposed both by Bez-Bardili and by Sanders (1939) involving the sample thickness and the frequency of the ultrasonic beam, namely, that the product of these should be greater than 4 cm. MC/S for equations (1) to be valid. But it is found in our investigation that as the thickness of the plate is increased, the critical angles decrease slightly and the velocities increase, approaching a limiting value for a thickness far less than that proposed above. To illustrate this point, the variation of the two velocities with thickness has been examined in the case of two metals and two rocks and the results given in Table I.

It is observed that in addition to the dip corresponding to the longitudinal waves, there are occasionally a number of other minima on each side which are usually less prominent. In some exceptional cases, it has even been found necessary to have a rough idea of the longitudinal velocity to identify the appropriate dip. This is particularly so with metals and does not occur with rocks. These spurious minima decrease with increasing thickness of the sample used.

This method, although it involves the use of somewhat large samples of material (3 cm. × 3 cm.), has the following advantages:

(i) the readiness and accuracy with which both torsional and longitudinal velocities may be determined:

(ii) the oscilloscope pattern can be used as a very sensitive peak voltmeter in judging the critical positions:

(iii) the original and received pulses can be separately observed on the oscilloscope and no elaborate screening of the original pulse is necessary.

3. Results and Discussion

Tables I and II give the variations in critical angles i_L and i_T and hence the velocities (V_L and V_T in m/sec.) with thickness (D in mm.) in the case

of copper, nickel, marble and shale. Young's modulus Y, rigidity modulus n in units of 10^{11} dynes/cm.^{2} and the Poisson's ratio σ have also been tabulated.

TABLE I

Material	D	i_L	i_T	V_L	V_T	Y	n	σ
Copper	1·05	19·0	52·8	4610	1886	8·86	3·17	0·400
	2·05	18·1	45·4	4832	2111	10·95	3·96	0·382
	3·00	18·1	43·0	4832	2204	11·81	4·32	0·368
	3·55	18·1	41·9	4832	2250	12·30	4·50	0·362
Nickel	1·40	17·5	38·5	4992	2412	13·80	5·12	0·348
	2·05	16·6	33·8	5255	2704	17·18	6·51	0·320
	2·85	15·0	31·0	5827	2913	20·14	7·55	0·330
Marble	2·00	12·6	35·3	6894	2600	5·52	1·95	0·417
	2·90	11·9	34·2	7297	2674	5·85	2·06	0·421
	3·45	11·8	33·3	7333	2737	6·11	2·16	0·416
Shale	1·00	16·9	50·7	5154	1937	3·27	1·15	0·418
	2·00	15·4	46·0	5650	2270	4·44	1·58	0·404
	3·25	15·5	46·0	5620	2270	4·43	1·58	0·403

In all the four cases, the ultrasonic velocities reach limiting values with increasing thickness. These limiting values represent the correct figures and they are compared in Table II with the results of Schneider and Burton

TABLE II

Material	Observer	D	V_L	V_T	Y	n
Copper	Authors	3·55	4832	2250	12·30	4·50
	Schneider and Burton	3·30	4820	2280	12·20	4·25
	Hand Book	..	..	..	12·06 to 12·85	4·24
Nickel	Authors	2·85	5827	2913	20·14	7·55
	Hand Book	..	..	..	20·01 to 21·38	7·06 to 7·55
Aluminium	Authors	1·15	6312	2688	5·42	1·95
	Schneider and Burton	1·04	6340	2620	5·18	1·85

and with those taken from *Hand Book of Chemistry and Physics* (1950–51). Results in Aluminium, which has been worked only at one thickness (1·15 mm.), are also compared with those obtained by Schneider and Burton for a similar thickness.

In this method it is possible to determine the critical angles to within 0·1°. Therefore the error in the determination of the longitudinal velocities will be in the range of 0·5 to 0·9 per cent., increasing as the velocity increases. The torsional velocities are determined with greater accuracy as the angles involved are much larger. Water is used as the tank liquid throughout and its velocity has been assumed to be 1503 m/sec. corresponding to a temperature of 27° C. It will be seen from Table II that there is good agreement between our results and those of the previous workers.

The method has been applied to the case of several Indian rocks and Table III gives the results obtained along with the density ρ.

TABLE III

No.	Name	Locality	D	ρ	i_L	i_T	V_L	V_T	Y	n	σ
1	Granite	Hyderabad	2·57	2·80	12·1	39·3	7157	2370	4·52	1·57	0·438
2	Quartzite	Manditog (Hyderabad)	2·04	2·56	15·9	30·9	5610	3030	5·31	2·35	0·294
3	Limestone	Hyderabad	3·05	3·00	13·9	29·7	6237	3018	7·36	2·73	0·348
4	Marble	Manditog (Hyderabad)	3·45	2·88	11·8	33·3	7333	2737	6·11	2·16	0·416
5	Deccantrap	Igadpuri (Bombay)	2·50	3·10	12·6	28·1	6866	3188	8·59	3·15	0·364
6	Shale	Hyderabad	3·25	3·07	15·5	46·0	5620	2270	4·43	1·58	0·403
7	Dolerite	Hyderabad	4·00	3·12	13·1	27·1	6621	3310	9·12	3·42	0·333
8	Schist	Hyderabad	1·65	2·97	13·6	31·8	5964	2852	6·54	2·42	0·352
9	Khondolite	Waltair	1·20	2·60	17·8	44·6	4894	2198	3·26	1·17	0·385
10	Charnokite (Acid)	Madras	2·50	2·64	11·5	27·4	7575	3268	8·81	2·82	0·386
11	Rhyolite	Sujargarh (Bikaneer)	4·56	2·75	12·4	28·1	6990	3190	7·66	2·80	0·368
12	Sodalite Syenite	Kishengarh (Rajasthan)	4·25	2·52	13·5	33·5	6448	2793	5·45	1·97	0·384
13	Nephelene Syenite	Sivamalai (Madras)	4·35	2·70	14·1	33·1	6160	2754	5·64	2·05	0·376

In the above table, rocks 1 to 4 have also been investigated by the wedge method by one of the authors (1953). Results obtained in the two methods are compared in Table IV and it is seen that there is satisfactory agreement.

TABLE IV

No.	Rock	Wedge V_L	Wedge V_T	Pulse V_L	Pulse V_T
1	Granite	7078	..	7157	2370
2	Marble	7500	3245	7333	2737
3	Quartzite	5630	3151	5610	3030
4	Limestone	6212	3100	6237	3018

It has been pointed out in an earlier paper by one of us (1952) that transmission of sound is clearly related to the granular texture and mineralogical composition of the rock specimen under investigation. A similar phenomenon has been observed in this investigation in respect of the intensity of the transmitted pulse. Thus the more homogeneous rocks like Limestone, Marble and Rhyolite transmit the sound beam without much fall in intensity unlike the non-homogenous rocks like Granite, Khondolite and Dolerite. A quantitative study of the texture of the rocks and their transmission properties is under progress.

4. SUMMARY AND CONCLUSION

The phenomenon of total internal reflection has been employed in developing a technique for measuring the ultrasonic velocities in solids using pulsed ultrasonic beams. The ease and accuracy with which the critical angles can be measured make this method superior to other methods in some respects. Besides the longitudinal velocities, torsional velocities have also been measured in a number of Indian rocks for the first time. It is essential to use fairly large sized samples in this method. An earlier observation indicating a dependence of sound transmission on granular texture of the rocks has been confirmed qualitatively in this investigation as well.

In conclusion, the authors desire to express their grateful thanks to Professor S. Bhagavantam for his guidance and helpful suggestions throughout this work.

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STUDIES ON THE NATURE OF THE RACEMIC MODIFICATIONS OF OPTICALLY ACTIVE COMPOUNDS IN THE SOLID STATE

Part X. *o*-, *m*-, *p*-Chloroanilino-camphor-β-sulphonates (*d* and *dl*) and Camphor-β-sulphonyl-*o*-,-*m*-, *p*-chlorophenylamides (*d* and *dl*)

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THE present communication is a continuation of our work described in Part IX[1] and deals with the comphor-β-sulphonates (*d* and *dl*) of *o*-, *m*-, *p*-chloraniline and camphor-β-sulphonyl-*o*-, *m*-, *p*-chlorophenylamides (*d* and *dl*). It is well known that a recemic modification of an optically active compound may occur in 3 forms: (i) *racemic conglomerate* or *mixture* of *d*- and *l*-isomers in equal molecular proportions (Type I); (ii) *racemic compound* (*dl*) composed of one molecule of each of the optical and opposite isomers (Type II); and (iii) *racemic solid solution* or *mixed crystals* of equimolecular proportions of *d*- and *l*- forms (Type III). In general racemic compounds appear to be more common than either conglomerates or solid solutions.

There are 3 methods for distinguishing these different forms: two of them, due to Roozeboom,[2] based on phase rule, employ (*a*) the freezing-point (melting point)-composition diagrams and (*b*) solubility-composition diagrams. The third method, due to Singh,[3] is the Biochemical. We have employed the melting-point-composition diagrams for the elucidation of the racemic modifications of the above mentioned compounds. In each case the diagram consisted of 3 curves, thus establishing the racemic form to be true *dl*-compound.

The melting-point-composition diagrams for the 6 pairs of compounds are given in Figs. 1-6.

In the case of " ideal " substances, it is possible to calculate the freezing-point (melting-point) lowering of the solvent by the addition of a solute in a binary mixture according to the freezing-point equation.

The freezing-point equation.—A pure substance (A) gives generally a sharp melting-point which is usually lowered by the addition of another substance (B) soluble in it. The extent of the lowering depends on several

variable factors and may be calculated by making certain assumptions. If the two components of a binary mixture form an "ideal" solution, the additive properties of the solution are linear functions of its composition as in Raoult's law which may be stated thus: *The escaping tendency of any chemical species is proportional to its mole fraction*:

$$p/p_0 = N_A \tag{1}$$

where p_0 = partial pressure of pure A,

and N_A = Mole fraction of A $= \dfrac{\text{moles of A}}{\text{total number of moles in mixture}}$

The approximate form of the Clausius-Clapeyron equation, deduced from the second law of thermodynamics, as applied to a liquid mixture in equilibrium with crystals of pure A, is given by the following expression (2):

$$dl_n(p) = \frac{L_f}{RT^2}\,dT \tag{2}$$

where $l_n = \log_e$,

p is the partial pressure of component A, L_f is its molar heat of fusion, R is the ideal gas constant, T is the equilibrium temperature in degrees absolute. The lowering of the freezing-point or melting-point of component A by the addition of another substance (B) soluble in it can be determined by integrating this equation between the limits of T_0 to T and p_0 to p respectively, T_0 and p_0 being the freezing-point and partial pressure of pure A. Thus if L_f is constant, we obtain

$$l_n(p/p_0) = \frac{L_f}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) = -\frac{L_f(T_0 - T)}{RTT_0} \tag{3}$$

Combining Raoult's law (1) with equation (3), we may write

$$l_n N_A = -\frac{L_f(T_0 - T)}{RTT_0}$$

Substituting ΔT for $T_0 - T$ = lowering of freezing-point of A, we finally obtain

$$\Delta T = -\frac{RTT_0}{L_f}\,l_n N_A \tag{4}$$

In the derivation of this simplified freezing-point equation (4), describing the extent of freezing-point lowering caused by impurity (B) dissolved in A, the following assumptions are made:—

(i) that the vapour over the liquid and solid at equilibrium behaves as an ideal gas within the temperature and pressure ranges involved; (ii) that

the volume of liquid and solid phases is negligible in comparison with the corresponding volume of vapour; (iii) that L_f is a constant over the temperature range considered; and (iv) that the components of the mixture are mutually ideal, in other words, that the intramolecular forces are the same in both components of the mixture. It may be assumed that close to the melting-point where the pressure of the vapour is small, conditions (i) and (ii) may be expected to hold. The latent heat of fusion (iii) mentioned above does not vary much over a small range of temperature.

Intramolecular forces may thus be the main cause for the deviations from Raoult's law. The dextro and lævo isomers possess the same energy, but the racemic compound (*dl*) has generally different energy content to which we must ascribe deviations from the freezing-point equation. The lowering of the freezing-point can be calculated from the freezing-point equation. Any deviation from the theoretical value of the lowering of freezing-point can be accounted for in simple cases, but often on account of the system being too complicated or its behaviour not being understood, no explanation is possible.

A few of the commoner causes for these deviations are discussed below:

(1) *The solute molecules may form polymers.*—The number of effective molecules of the solute will be reduced, consequently the lowering of the freezing-point of the solvent will be less than that for ideal cases. So far no experimental evidence is available for suggesting that *d*-, *l*- and *dl*-isomers exist as dimers or trimers.

(2) *The solute molecules* (dl) *dissociate into* d *and* l *molecules* (curves DE_1, Figs. 1–6).—If the solute molecules dissociate, their mole fraction will not increase but that of the solvent (*d*) will increase depending on the extent of dissociation of the solute, so that the observed depression of the melting-point of the solvent (*d*) will be less than that predicted from the freezing-point equation. As the solvent (*d*) is one of the products of dissociation, according to the law of mass action, it will act in the opposite direction and reduce dissociation. This makes the system not only complicated but its behaviour is not sufficiently known. In the case of chloranilino-camphor-β-sulphonates, the DE_1 curves are of 3 types: the curve of the *ortho*-compound (Fig. 1) is convex, that of the *meta* derivative (Fig. 2) is a straight line and that of the *para*-isomeride (Fig. 3) is concave to the composition axis.

(3) *The solvent molecules* (dl) *dissociate into* d *and* l *molecules* (curves RE_1, Figs. 1–6).—If the solvent molecules dissociate, their effective mole

fraction will decrease and that of the solute molecules will increase: this will give a greater lowering of freezing-point than that predicted for the ideal case. The addition of the solute molecules (*d*) will, according to the law of mass action, reduce the degree of dissociation and thus act in the opposite direction. These opposite reactions thus make the system complicated. The isomeric camphor-β-sulphonates give 3 kinds of curves (RE_1): the *meta*-compound (Fig. 2) gives an interesting curve with a point of inflexion (I_1), below which the curve (E_1I_1) is concave and above it, convex (I_1R) to the composition axis.

Camphor-β-sulphonyl o-, m-, p-*chlorophenylamides*.—The position isomerides give different kinds of curves (RE_1, Figs. 4, 5 and 6): the *meta*-compound (Fig. 5) gives a straight line, the other two being convex curves. The *para*-compound (Fig. 6) is interesting as the melting point of the *d*-isomeride (curve DE_1) is not depressed by the addition of the *dl*-compound over the considerable range of 50 per cent. to 20 per cent. This is contrary to expectations based on the freezing-point equation. It clearly, however, indicates the formation of solid solutions or mixed crystals between the dextro and the racemic isomeride in this region. This point will be further discussed in the next section.

Discussion on the Nature of Racemic Modification with the Aid of the Melting Point-Composition Diagrams

(Figs. 1–6)

The diagrams were prepared as described in the previous communication[1]: the *d-dl* and *dl-d* diagrams are given in firm curves; their mirror images are indicated in broken curves. The melting point-composition diagrams (Figs. 1–6) consist of 3 curves with a central maximum which shows that the racemic forms are true *dl*-compounds. The following criteria are employed in the *qualitative* discussion of these Roozeboom diagrams: If the central portion of the curve is steep, the racemic compound is stable; if it is flattened the racemic compound is unstable and is split up into its active components (*d* and *l*) at its melting-point depending upon the degree of dissociation. The area occupied by the central portion of the diagram gives the range of the stability of the racemic compound. If the minima or eutectic points are sharp and well defined, the racemic compound and the active isomer do not form solid solutions, whereas if the eutectic points are not sharp and well defined and the curves are continuous in the region near the eutectic points, it indicates the formation of mixed crystals or solid solutions between the active and the racemic compound:

dl-o-*Chloroanilino-camphor-β-sulphonate* (*Fig.* 1).—The *dl-d*-curve (RE_1) is fairly steep which shows that the racemic compound is fairly stable.

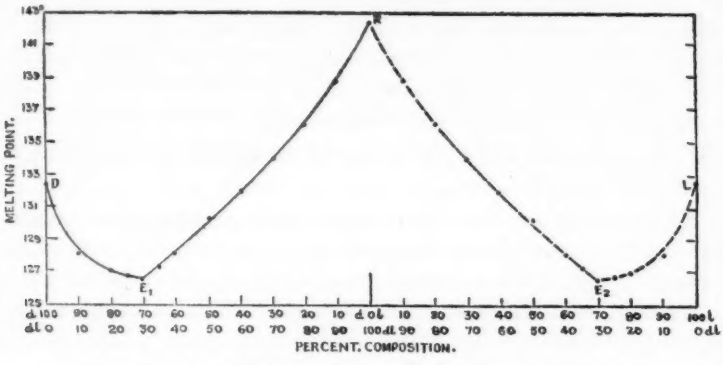


FIG. 1. *o*-Chloroanilino-camphor-β-sulphonates.

The eutectic point (E_1) is sharp which indicates that the *d* and *dl* compounds do not form solid solutions in this region.

dl-m-*Chloroanilino-camphor-β-sulphonate* (*Fig.* 2).—The *dl-d* curve (E_1I_1R) is interesting: it exhibits a point of inflexion (I_1) below which the curve (E_1I_1) is concave to the composition axis and above it (I_1R) convex.

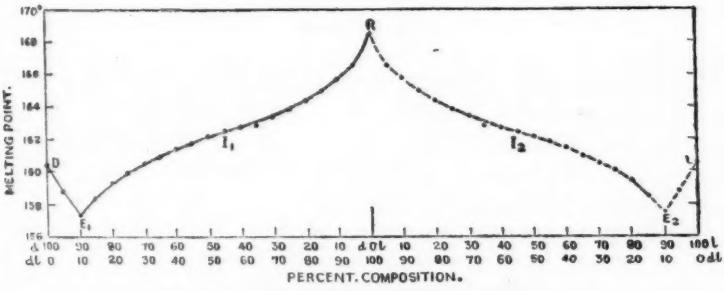


FIG. 2. *m*-Chloroanilino-camphor-β-sulphonates.

It shows that the variable factors which determine the deviation of the curve from the " ideal " case operate in opposite directions in these segments. The system is, therefore, too complicated for elucidation as its behaviour is not sufficiently known. The eutectic points (E_1, E_2) are sharp. The curve *d-dl* (DE_1) is a straight line. The per cent. composition of the eutectic point (E_1) is 90 *d*: 10 *dl*. This shows that the range of stability of the racemic compound is very large extending from 10 per cent. *dl* to 100 per cent. *dl*.

dl-p-*Chloroanilino-camphor-β-sulphonate* (*Fig.* 3).—The curve *dl-d* (RE_1) is fairly steep and slightly concave to the composition axis. The *d-dl* curve (DE_1) is also concave and fairly steep. The eutectic point (E_1)

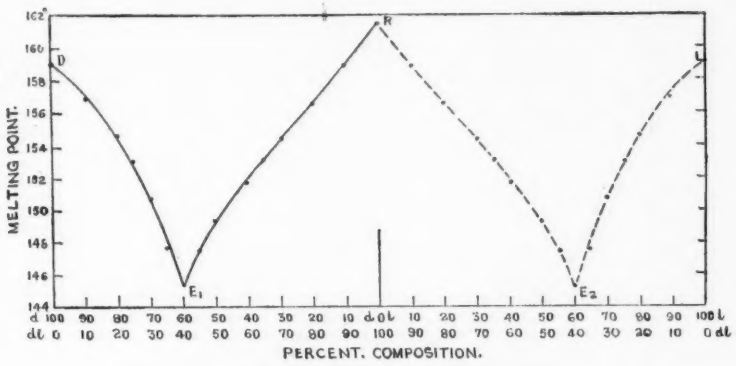


FIG. 3. *p*–Chloroanilino-camphor-β-sulphonates.

is very sharp which indicates that there is no tendency between the *d-* and *dl-*isomers to form solid solutions. The percentage composition corresponding to the eutectic point is 60 *d*: 40 *dl*. The racemic compound is fairly stable and does not appear to be appreciably dissociated into its optical and opposite isomers. Its range of stability is fairly large.

dl-*Camphor-β-sulphonyl-o-chlorophenylamide* (*Fig.* 4).—The *dl-d* curve (RE_1) is not steep but considerably flattened, which shows that the racemic

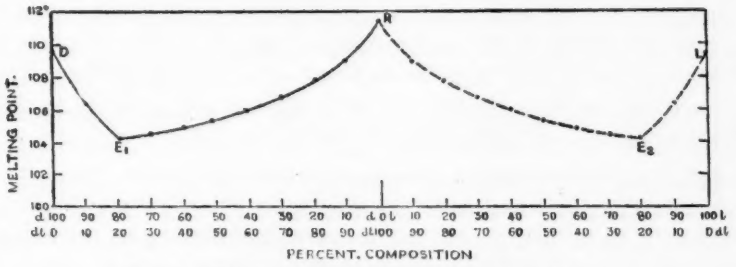


FIG. 4. Camphor-β-sulphonyl-*o*-chlorophenylamides.

compound is largely dissociated. Its range of existence is, however, fairly large, namely, from 20 per cent. *dl* to 100 per cent. *dl*. The eutectic point is fairly well defined, corresponding to the composition of the mixture as 80 per cent. *d*: 20 per cent. *dl*.

dl-*Camphor-β-sulphonyl*-m-*chlorophenylamide* (*Fig.* 5).—The *dl-d* curve (RE_1) is a straight line and fairly steep; the racemic compound is, therefore,

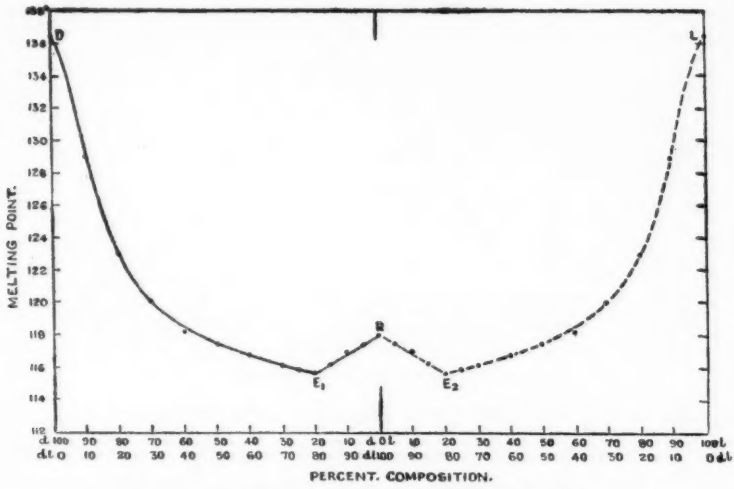


FIG. 5. Camphor-β-sulphonyl-*m*-chlorophenylamides.

stable, but its range is very limited, namely, 80 per cent. *dl*: 100 per cent. *dl*. The eutectic point is sharp and corresponds to 20 per cent. *d*: 80 per cent. *dl* in composition. It is interesting to note that the addition of 10 per cent. of the *dl*-form to the pure *d*-component lowers its melting-point by 7·5°, whereas the addition of the same amount of the *dl*-compound to the mixture consisting of 30 per cent. *d* and 70 per cent. *dl* produces a remarkably small lowering in its melting-point, namely, 0·5°. The *d-dl* curve (DE_1) is, therefore, very steep in its initial course. This points to the fact that the deviations from the freezing-point equation are governed by different variable factors at different points of the curve (DE_1).

dl-*Camphor-β-sulphonyl*-p-*chlorophenylamide* (*Fig.* 6).—The *dl-d* and *dl-l* curve (E_1RE_2) is flattened, showing some dissociation of the racemic compound at its melting-point. As this curve also shows a central maximum, the racemic form is a definite compound, but its range is small. The eutectic points (E_1 and E_2) are very ill-defined and the curves are continuous in these regions extending from 50 per cent. of *d*-form to 20 per cent. of this isomeride in the mixture. This clearly shows the formation of mixed crystals or solid solutions without any lowering in the melting-point in spite of such marked change in composition of the mixture. Such solutions do not obey the

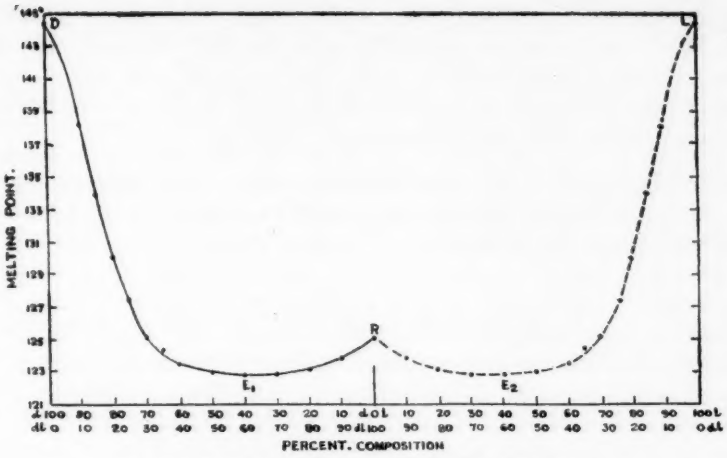


FIG. 6. Camphor-β-sulphonyl-*p*-chlorophenylamides.

freezing-point equation, and the solvent (*d*) and the solute (*dl*) both separate out together as mixed crystals in this region. The *d*-*dl* curve (DE_1) behaves in a similar way to that of the *meta*-compound already discussed.

THE EXISTENCE OF THE RACEMATES IN THE (*a*) SOLID, (*b*) LIQUID AND (*c*) GASEOUS STATE

(*a*) *Solid state.*—Pasteur[4] held that the occurrence of hemihedral faces in crystals was a sufficient criterion for an optically active substance, whereas he considered that the racemic form should be holohedral. Later experience has shown that hemihedry in crystals is not a necessary or constant expression of optical activity. There were also other rules which were found to be equally unstatisfactory.

Roozeboom[2] employed phase rule as a guide in determining the nature of racemic substances in the solid state. He put forward, from theoretical considerations, the solubility-composition and fusion-composition diagrams of mixtures of optically active and inactive isomers for the diagnosis of the nature of the racemic form of the substances.

In an earlier section of this paper the melting point-composition diagrammatic method has been described and with its aid it was established that the 6 compounds described herein are true racemic (*dl*) compounds. Many similar instances of racemic compounds have been described in previous parts of this series.[5] The results of this method are however valid at or near the melting-point of the compounds.

The theoretical solubility-composition diagrams given by Roozeboom[2] and by Bruni[6] were not established experimentally till one of the present writers provided these diagrams in the case of camphoric acids,[7] camphor-β-sulphonic acids,[8] and camphorcarboxylic acids[9] and thus correlated these solubility curves with the melting-point diagrams.

(*b*) *Liquid state.*—The existence of racemic compounds in the liquid state has long been debated among physical chemists. Many methods have been suggested to decide whether a racemate on fusion or in solution is converted into a mixture of the *d*- and *l*-forms or whether it exists as a compound (*dl*). Ladenburg[10] mixed *d*-conine and *l*-conine in equimolecular proportions and observed development of heat. He concluded that the opposite and active conines combined to form *dl*-conine in the liquid state. Most chemists, however, do not agree with Ladenburg's conclusion. Ordinary cryoscopic methods fail to establish double molecular weights for racemates in solution which shows that they almost completely undergo dissociation in solution. The presence of one of the products of dissociation reduces the degree of dissociation: Walden[11] and Patterson[12] found that the molecular weight of racemic diacetyl tartrate when determined in presence of active diacetyl tartrate as the solvent was considerably greater than in water as the solvent. The absorption spectra of *d*-, *l*- and *dl*-tartaric acids in dilute solutions show no differences, whereas measurements in concentrated solutions lend undoubted support to the existence of racemic acid in solution: Stewart[13] found that the absorption spectra of similar solutions of dextro and racemic tartaric acids are identical at low concentrations, whereas they show distinct differences at higher concentrations (14 per cent.). Again the fact that the colour of Fehling's solution that is made from racemic acid is appreciably different from the colour of an equivalent solution which is made from *d*-tartaric acid strongly suggests that in racemic Fehling's solution the enantiomorphic forms are in some way combined with each other.[14]

Dunstan and Thole[15] from the examination of viscosity-concentration curves of the aqueous solutions of active and racemic tartaric acids showed that the amount of undissociated racemic acid increased with increasing concentration.

Singh[16] *et al.* determined the viscosity of *dextro*, *lævo* and *racemic* forms of several compounds at different concentrations, which lend strong support to the existence of racemates in concentrated solutions. They found that the viscosity-concentration curves of *d*- and *l*-forms were superposable for the whole range of concentrations investigated. The curves for the racemic

compounds were indistinguishable from those of the active forms at low concentrations indicating that the racemic compounds were completely dissociated into the optically active components. At higher concentrations the viscosity-concentration curves of the inactive and active forms diverge more and more apart which shows the presence of increasing amount of racemate in solution with increasing concentrations. The racemates having higher molecular weights give higher viscosity. The limits of concentration above which the curves of the racemates diverge apart from those of the active forms varies with the nature of the compound and the solvent as shown below:

dl-camphor: about 5 per cent. in ethyl alcohol;

dl-isonitrosocamphor: about 2·26 per cent. in ethyl alcohol;

dl-camphorquinone: about 20 per cent. in chloroform and about 7·7 per cent. in ethyl alcohol;

dl-sodium camphorate: about 9 per cent. in water;

dl-camphoric acid: about 10 per cent. in ethyl alcohol.

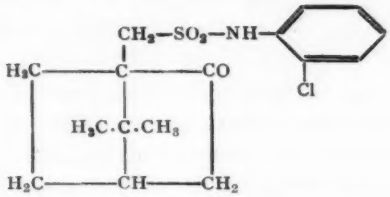
Although, as will be seen, some support has been adduced regarding the existence of racemic compounds in the liquid state, it seems that the only satisfactory evidence is that which is derived from Roozeboom's melting point-composition curves depending on the extent to which the maximum of the melting point-composition curve is rounded. In general the more rounded this maximum is, the greater is the dissociation of the compound into its components in the liquid phase at the melting-point. By means of this fact, Ross and Somerville[17] showed that the racemic camphoric acid dissociated upon melting to the extent of about 12 per cent. and similarly methyl hydrogen camphorate about 18 per cent.

Singh and Nayar[18] similarly found that camphorcarboxylic acid dissociated at its melting-point into its optically active components to the extent of about 27 per cent. It may be, however, noted that these results apply to temperatures at or near the melting-point, whereas at temperatures above their melting-points the liquid racemic substances always behave as mixtures.

(*c*) *Gaseous state*[19].—Unlike the solid and liquid racemates there is no evidence which supports the view that the racemic compounds exist in the gaseous state also.

EXPERIMENTAL

d-*Camphor-β-sulphonyl*-o-*chlorophenylamide*



Molecular proportions of *d*-camphor-β-sulphonylchloride, *o*-chloraniline (colourless) and dry pyridine were heated together at 100° C. in a water-bath using an air condenser for about 14 hours. On cooling a semi-solid mass was formed which solidified on the addition of water. It was filtered and dissolved in alcohol and precipitated by the addition of water. It was purified by repeated recrystallisations from rectified spirit (animal charcoal). Finally it was crystallised from 75 per cent. ethyl alcohol as colourless rectangular plates, melting at 109°–10° C. It is very easily soluble in benzene, acetone, chloroform, carbon tetrachloride, pyridine and ethyl acetate, fairly soluble in methyl alcohol and ethyl alcohol and insouble in water, petroleum ether and ether.

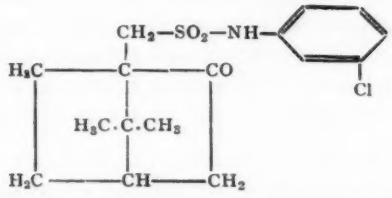
S (found) = 8·96 per cent.

dl-*Camphor-β-sulphonyl*-o-*chlorophenylamide* was prepared in the same way as the *d*-form using *dl*-camphor-β-sulphonylchloride and has similar properties and solubility. It was crystallised from 75 per cent. ethyl alcohol as colourless rectangular plates melting at 111·5° C.

S (Found) = 9·2 per cent.

$C_{10}H_{15}O.SO_2.HN.C_6H_4.Cl$ requires S = 9·4 per cent.

d-*Camphor-β-sulphonyl*-m-*chlorophenylamide*



Molecular proportions of *d*-camphor-β-sulphonyl chloride, *m*-chloraniline and pyridine, on being condensed and treated in the same way as in the previous case gave colourless needles, melting at 136·5° C. The compound

is easily soluble in benzene, acetone, chloroform and pyridine, and fairly so in ethyl alcohol, methyl alcohol and ethyl acetate and insoluble in petroleum ether, carbon tetrachloride and water.

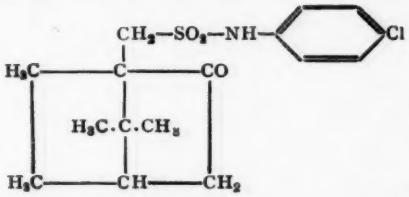
S (Found) = 9·45 per cent.

The *dl*-isomer was obtained similarly as colourless needles, melting at 118° C. Its solubility is similar to that of the *d*-form.

S (Found) = 9·09 per cent.

$C_{10}H_{15}O.SO_2.HN.C_6H_4.Cl$ requires S = 9·4 per cent.

d-*Camphor-β-sulphonyl*-p-*chlorophenylamide*



Molecular proportions of *d*-camphor-β-sulphonyl chloride, *p*-chloraniline (m.p. 60° C.) and dry pyridine on being treated in the same way gave on crystallisation a colourless compound as rectangular plates, melting at 144·5° C. It is easily soluble in chloroform, carbon tetrachloride, acetone, benzene, pyridine and ethyl acetate and fairly soluble in ethyl alcohol and methyl alcohol and insoluble in water, petroleum ether and ether.

S (Found) = 10·00 per cent.

The *dl*-compound was prepared in the same manner and obtained as colourless square shaped plates melting at 125° C.

Its solubility is similar to that of the *d*-form.

S (Found) = 8·98 per cent.

$C_{10}H_{15}O.SO_2.HN.C_6H_4.Cl$ requires S = 9·4 per cent.

o-, m- and p-*Chloranilino-camphor-β-sulphonates*

$(C_{10}H_{15}O.SO_3H.H_2N.C_6H_4Cl)$

d- and *dl*-camphor-β-sulphonates of *o*-, *m*- and *p*-chloraniline were prepared in the same manner as described by Singh and Perti.[20] The properties of these compounds were found to be same as given by them except in the case of the *m*-isomerides. The *d*-form melts at 160°–61° C. and not at 159

60° C. and the *dl*-isomer melts at 168°-69° C. and not at 164°–65° C., as given by them. The *dl*-form on analysis gave the following result:—

S (Found) = 9·15 per cent.

$C_{10}H_{15}O.SO_3H.H_2N.C_6H_4.Cl$ requires S = 8·9 per cent.

The melting point-composition diagrams were prepared as follows: An intimate mixture of known composition of the racemic form and the *dextro*-isomeride was prepared by taking exact weights of the components in different proportions in an agate mortar and thorough mixing and grinding. Six determinations of the melting-point (capillary tube method) of each mixture were made with Siebert and Kuhn thermometers graduated to 0·2° C. and the mean value was taken as the melting-point of the mixture. The results are plotted as melting point-composition diagrams in Figs. 1–6. The data giving melting-points and percentage composition by weight of different mixtures are omitted for the sake of economy of space.

SUMMARY

1. Roozeboom's melting point-composition diagrams have been prepared for the camphor-β-sulphonates (*d* and *dl*) of *o*-, *m*- and *p*-chloraniline and camphor-β-sulphonyl- *o*-, *m*- and *p*-chlorophenylamides (*d* and *dl*). Three curves were obtained in each case which showed that they were true *dl* compounds.

2. A freezing-point equation has been developed. The above mentioned Roozeboom curves have been discussed in relation to the ideal case as given by this equation. It is found that the systems represented by these curves are complicated as their behaviour is not sufficiently understood.

3. The stability of these compounds has been discussed with the aid of Roozeboom's melting-point diagrams.

4. The existence of racemates in solid, liquid and gaseous states has been discussed.

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FINE STRUCTURE IN THE DIRECTIONAL INTENSITY OF COSMIC RAYS AT HYDERABAD

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1. Introduction

The presence of prominences and depressions in the zenith angle-intensity distribution curve for cosmic rays is explained in certain cases as due to the banded nature of the penumbra, *i.e.*, the presence of regions of allowed and forbidden energy bands (Schremp, 1938). In addition to this, considerations of absorptive effects also assume importance in explaining this phenomenon.

The first experimental evidence of fine structure was reported by Cooper and by Ribner in 1939 and by Schremp and Banos in 1940. Cooper found at Missouri ($\lambda = 49°$) three approximately symmetrical prominences in all the eight principal azimuths about the zenith at $\theta = 7°$, 20° and 37° where θ is the zenith angle. Ribner got one pair of symmetrical prominences at 20° with an indication of peaks at 10° and 40° in both the east and west azimuths. The experiments of Schremp and Banos at Mexico ($\lambda = 29°$) also revealed the presence of fine structure beyond any doubt. The detailed study of Yeater (1945) brought out the presence of symmetrical prominences at 5°, 20° and 40° in the four principal azimuths. Cocconi and Tongiorgi (1946) performed their experiments at Milan ($\lambda = 49°$, $h = 2200\ m$) and they have concluded that their measurements both with lead absorbers and with varying zenith angle on the intensity variation of the mesonic component of cosmic radiation do not confirm the existence of fine structure in the absorption curves. Bhattacharya (1942) reported the existence of fine structure at Calcutta ($\lambda = 12°$ N). Om Parkash (1950) studied fine structure for both the eastern and western azimuths at Lahore ($\lambda = 22°$ N).

As pointed out by Vallarta (1939) the effect of penumbra is significant at intermediate latitudes, namely 10° to 40°. But the work of Cooper and Ribner shows its influence beyond 40° (*loc. cit.*). Also the azimuthal symmetry of the fine structure observed in their measurements has been explained as due to a discrete energy spectrum of primary particles showing up as a result of the "Main cone" in approximate directions in the sky. Further, the studies of azimuthal variation of cosmic ray intensity at constant zenith

angle provide an excellent method of determining the energy spectrum of the primary particles [Bhowmik and Bajwa (1952); Gill (1947); Vallarta, Perusquia and De Oyarzabal (1947)].

In all the above quoted work, the presence of fine structure at low latitudes has not been much investigated, the exception being Bhattacharya (*loc. cit.*) at Calcutta ($\lambda = 12°$). He explored only the western azimuth. On the other hand, Schremp and Ribner (1939) have shown the apparent absence of fine structure at the equator from Johnson's (1935) experiments at Peru. Hyderabad having its $\lambda = 7{\cdot}7°$ N offers a low latitude station for such investigations. Advantage is taken of this and the present study of the fine structure in the intensity distribution in the east-west azimuths is undertaken.

2. Experimental Arrangement

Two cosmic ray telescopes are used in the present work. Each consists of three self-quenched G.M. Counters, mounted in parallel positions on a light wooden frame. For the studies in the eastern azimuth, the telescope subtends 9° 38′ in the zenith and about 85° in the lateral plane, the G.M. Counters being 38 cm. long and 3·5 cm. in diameter with 41·5 cm. between the two extreme counters. For studies in the western azimuth, the resolving power of the telescope is increased. It subtends an angle of 5° 18′ in the zenith, and about 56° in the lateral plane, the G.M. Counters being 40 cm. long and 3·5 cm. in diameter with a separation of 75·5 cm. between the two extreme counters. There is no special significance attached to the use of telescopes with different angles of opening for the eastern and western azimuths and they were thus used because they were made on different occasions with different dimensions. A triple coincidence circuit (Murty, 1953) is used after its thorough discrimination against singles and doubles. Readings are taken in both azimuths starting from the vertical upto 45° in steps of 5°. The telescope is kept for 15 minutes at each zenith angle each time. Observations are made by the method of cycles to minimise the effects of changes in the barometer conditions and changes in the intensity of the magnetic field of the earth. By completing in a relatively short time a cycle of the angles in the azimuth under study, these factors which are beyond experimental control remained essentially constant during the cycle. The total number of counts at each position was calculated and reduced to a common temperature of 30° C. and a pressure of 71 cm. of mercury, using the constants, $T_{N\theta} = -0{\cdot}18 \pm 0{\cdot}011$ per cent. per degree K and $T_{Nb} = -3{\cdot}45$ per cent. per cm. Hg, where $T_{N\theta}$ and T_{Nb} are temperature and pressure correction factors respectively (Janossy, 1950). The idea in applying these corrections is to bring about uniformity among all the cycles, in the azimuth

concerned, taken under different atmospheric conditions. It may be mentioned in this connection that the contribution of these corrections towards fine structure is very small.

3. Results and Discussion

At sea-level the zenith angle intensity curve is represented by the square of the cosine of the zenith angle. The observed anomalies which may be considered as deviations $\Delta(\theta)$ from the empirical curve $I(\theta) = I_0 \cos^2\theta$ or $I_0(\theta) = I(\theta) \sec^2\theta$ are presented in Fig. 1. The quantity $\Delta(\theta)$ plotted here is the per cent. deviation of $I_0(\theta)$ $[= I(\theta) \sec^2\theta]$ from the mean value of $I_0(\theta)$ over all angles. This type of representation flattens out the distribution curve and shows any prominences and depressions as oscillatory about a perfect cosine square distribution. The results are given in Table I. The probable errors (σ_c) are calculated from the number of counts and have been also computed from the residuals (σ_r). The relative magnitudes of the two sets of probable errors provide a criterion for judging the reliability of the counter-telescope. Of these two sets of values the probable errors from residuals are the more significant. The counting rates at the vertical given in Table I differ due to the difference in the geometry of the telescopes used. In Fig. 1 curves I and II correspond to east and west azimuths at Hyderabad, and curve III plotted from the results of Bhattacharya (*loc. cit.*) for the western azimuth at Calcutta. The arrows show the extent of probable errors.

All the curves in Fig. 1 show the conspicuous prominence at about 40° which has been reported by previous workers. There are two humps at about 10° and 30° in curve I and one at about 20° in curve II. The prominence near the zenith is indicated in all the curves. Further, two depressions in the east one at about 25° and the other at 35° and one depression at 25° in the west are also present at Hyderabad. Curve II and curve III show a general correspondence between the results at Calcutta and at Hyderabad. The depression at 30° and the peak at 25° at Calcutta are observed at 25° and 20° respectively at Hyderabad. Thus the results show beyond any doubt the existence of fine structure even at such a low geomagnetic latitude as 7·7° N.

From the earliest days of the prediction and consideration of fine structure, the symmetry it shows has been taken as the key to its interpretation (Warren, 1946). Irregularities caused by atmospheric absorption should depend only on the length of the atmospheric path traversed, and therefore be independent of azimuth. The effect of the earth's magnetic field is not expected to show any such symmetry. The symmetrical deviations about the zenith, namely a prominence at about 40° and a depression at about 25°,

may be attributed to the absorption effects associated with a traversal of range limits of lines or bands in the energy spectrum of the primary cosmic rays. The asymmetrical prominence at about 10° in curve I may be due to magnetic effects associated with the edges of the main cones and the penumbral bands of the Lemaitre and Vallarta theory (1936).

TABLE I

Fine structure data in the eastern and western azimuths at Hyderabad (7·7° N) India

Zenith-angle θ	Time in minutes T	Total counts C	Counts per minute C/T $\pm$ *p.e.*	Per cent. deviation $\Delta(\theta)$	Probable errors from counts σ_e	Probable errors from residuals σ_r
East						
0°	1050	5423	5·163 ± ·047	+ ·036 (×100)	·009	·010
5°	810	3963	4·893 ± ·053	− ·011	·011	·012
10°	825	4015	4·865 ± ·052	+ ·006	·011	·012
15°	825	3815	4·624 ± ·050	− ·006	·011	·011
20°	810	3477	4·292 ± ·049	− ·025	·011	·012
25°	810	3222	3·978 ± ·047	− ·028	·012	·016
30°	825	3041	3·685 ± ·045	− ·014	·012	·014
35°	810	2601	3·211 ± ·042	− ·040	·013	·013
40°	810	2488	3·072 ± ·042	+ ·050	·014	·015
45°	810	2086	2·575 ± ·038	+ ·033	·015	·016
West						
0°	975	2008	2·059 ± ·031	− ·029	·015	·017
5°	720	1359	1·888 ± ·035	− ·103	·019	·020
10°	705	1308	1·855 ± ·034	− ·098	·018	·020
15°	705	1323	1·877 ± ·035	− ·051	·019	·019
20°	690	1243	1·799 ± ·034	− ·040	·019	·021
25°	675	1108	1·642 ± ·033	− ·058	·020	·021
30°	690	1094	1·586 ± ·032	− ·003	·020	·020
35°	690	1090	1·580 ± ·032	+ ·110	·020	·022
40°	660	951	1·441 ± ·032	+ ·158	·022	·024
45°	690	814	1·180 ± ·028	+ ·113	·024	·024

Another important characteristic of the anomalies caused by absorption is that any increase in the absorbing path, *i.e.*, in the zenith angle, can only decrease the intensity but would never increase it as is observed in the case of present anomaly at 25°.

Further studies in the case of other principal azimuths are in progress, as they provide data for a complete analysis of the primary rays, their spectra and their behaviour under absorption.

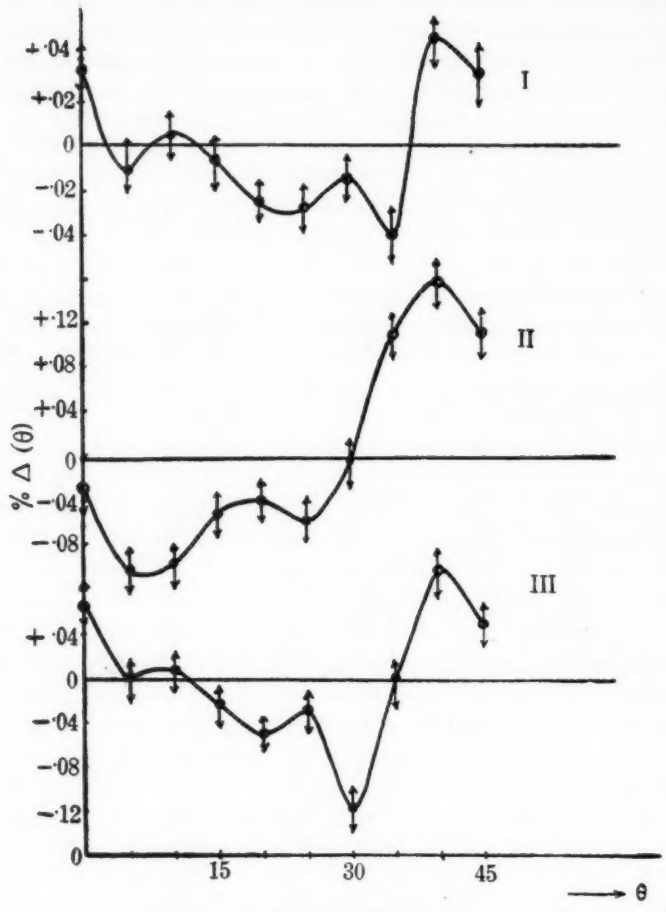

FIG. 1. $\Delta(\theta)-\theta$ graph
Curve I Eastern Azimuth, Hyderabad.
Curve II. Western Azimuth, Hyderabad.
Curve III. Western Azimuth, Calcutta.

The author offers his grateful thanks to Prof. S. Bhagavantam for his helpful guidance and constant encouragement in the progress of the present work.

4. SUMMARY

Fine structure measurements are taken at Hyderabad ($\lambda = 7{\cdot}7°$ N) in both the east and west azimuths. Two triple coincidence telescopes making

angles of 9° 38′ and 5° 18′ in the zenith, in the eastern azimuth and western azimuth respectively are employed. The observations are taken in steps of 5° from the vertical upto 45°. The results show the existence of fine structure for the first time at such a low geomagnetic latitude as 7·7° N.

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THE DECOMPOSITION OF HYDROGEN PEROXIDE BY POTASSIUM FERROCYANIDE

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It has been reported in an earlier communication[1] that the dark reaction between hydrogen peroxide and a pure dilute aqueous solution of potassium ferrocyanide is really due to the action of the former on potassium aquo-pentacyanoferrite, which exists as a substitution product in very minute concentration in aqueous solutions of ferrocyanide in the dark. Further it has been observed[2, 3] that the marked photochemical after-effect in H_2O_2-$K_4Fe(CN)_6$ reaction is due to the enhanced concentration of the aquo-salt (II) due to its photo-formation from ferrocyanide. Its magnitude has been found to depend on the period of pre-illumination of the H_2O_2-$K_4Fe(CN)_6$ reaction mixture.[4]

In the present paper the photochemical after-effect has been studied by separately pre-illuminating the ferrocyanide solution and adding it to hydrogen peroxide in the dark. Experimental results obtained by employing M/64·2 potassium ferrocyanide pre-illuminated by sunlight for two and five minutes have already been recorded.[3] These experiments show that within these limits of variation, the time of pre-illumination of potassium ferrocyanide produces no appreciable change in the after-effect.

Separate Pre-illumination of Potassium Ferrocyanide by Sunlight

In the following experiments, M/64 aqueous potassium ferrocyanide (10 c.c.) was exposed to sunlight for various time intervals 'T' and added to hydrogen peroxide in the dark immediately after exposure. The total volume of the reaction mixture was 50 c.c., and the concentrations of hydrogen peroxide and potassium ferrocyanide in the reaction mixture were N/6 and M/320 respectively. The velocity constant, K, has been calculated according to the unimolecular formula $K = 1/t \log a/a - x$, where 't' is the time in minutes, 'a', the initial concentration of hydrogen peroxide in terms of c.c. of potassium permanganate, and 'x', the change in time 't'. The amount of permanganate used up by ferrocyanide has been subtracted from the total volume used up in each titration. The technique adopted in this

investigation has been described in detail in an earlier paper. The temperature of the experiments was in all cases 40° C. As already reported,[1] $K \times 10^5$ for the dark reaction with unilluminated ferrocyanide = 35. This dark reaction has been recently critically examined by the author under various conditions.[4]

TABLE I
T = 10 *sec.*

t	*a*−*x*	K.10⁵
0	20·30	..
29	18·15	168
74	14·85	183
128	12·40	167
199	9·45	167
342	6·10	153

TABLE II
T = ½ *minute*

t	*a*−*x*	K.10⁵
0	20·30	..
26	17·70	229
70	13·70	244
124	9·80	255
196	6·30	259
338	2·60	264

TABLE III
T = 1 *minute*

t	*a*−*x*	K.10⁵
0	20·40	..
15	17·60	427
35	14·50	424
80	8·70	463
136	4·50	483

TABLE IV
T = 2 *minutes*

t	*a*−*x*	K.10⁵
0	20·50	..
15	18·20	345
30	16·50	314
60	12·90	335
126	7·25	358
180	4·55	363
243	2·55	373

TABLE V
T = 5 *minutes*

t	*a*−*x*	K.10⁵
0	20·50	..
25	18·70	267
31	17·10	254
60·5	14·05	271
123	9·00	291
189	5·85	288

TABLE VI
T = 10 *minutes*

t	*a*−*x*	K.10⁵
0	20·65	..
15	19·40	181
35	18·10	164
79	15·40	161
156	11·60	161

TABLE VII
T = 30 *minutes*

t	*a*−*x*	K.10⁵
0	20·10	..
40	18·50	90
85	16·50	101
132	14·70	103
210	11·80	110

TABLE VIII
T = 60 *minutes*

t	*a*−*x*	K.10⁵
0	20·00	..
23	19·20	77
72	17·30	88
132	15·10	92
192	13·40	91

The above experiments (Tables I-VIII) with M/320 potassium ferrocyanide pre-illuminated by sunlight over widely varying periods of time reveal a marked increase in the after-effect in the beginning with a subsequent rise to a maximum, followed by a gradual decrease with increasing periods of insolation of potassium ferrocyanide. These results have been illustrated in Fig. 1.

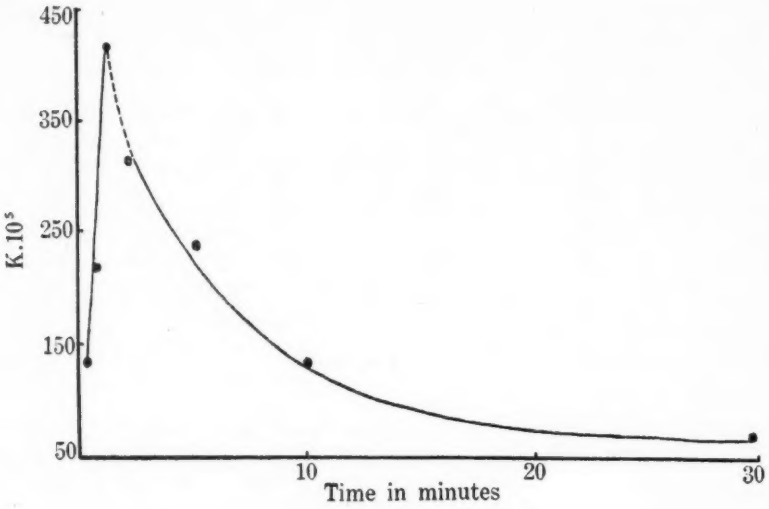

FIG. 1

Experiments were also conducted with M/64·2 potassium ferrocyanide using sunlight as the pre-illuminant as before. In these experiments, M/12·84 potassium ferrocyanide (10 c.c.) was insolated for various time intervals, 'T', and then mixed with hydrogen peroxide in the dark as soon as practicable after insolation. The total volume of the reaction mixture was 50 c.c. The strength of ferrocyanide in the reaction mixture was thus M/64·20. The concentration of peroxide in this mixture was N/6.

The experiments with M/64·2 potassium ferrocyanide (Tables IX-XII) therefore, confirm these observations, although the effect of long exposures on concentrated solutions is not as pronounced as on dilute solutions.

PRE-ILLUMINATION OF FERROCYANIDE BY LAMP LIGHT

Experiments were further carried out with solutions of M/320 potassium ferrocyanide pre-illuminated by the light of a 500 watt filament lamp operated on 220 volts. M/64 potassium ferrocyanide (10 c.c.) was irradiated by lamp

TABLE IX

T = 1 *minute*

t	*a*−*x*	K.10⁴
0	19·90	..
16	7·90	195
29	4·50	192
45	2·10	197

TABLE X

T = 5 *minutes*

t	*a*−*x*	K.10⁴
0	19·60	..
11	10·80	235
23	5·70	233
38	2·50	235

TABLE XI

T = 10 *minutes*

t	*a*−*x*	K.10⁴
0	19·70	..
13	10·00	227
27	4·85	225
35·5	3·10	226
50·5	1·30	234

TABLE XII

T = 20 *minutes*

t	*a*−*x*	K.10⁴
0	19·80	..
9	13·50	185
17	9·70	182
25	7·10	178
36	4·45	180

light placed at a distance of 40 cm. for various time intervals ' T ' and added to hydrogen peroxide in the dark as usual.

When sunlight is used for illumination, the after-effect rates are higher, the longer the exposure. This holds true up to a limiting period of illumination (one minute), and if the exposure is continued beyond this period, the after-effect rates show a decrease with increasing periods of irradiation. The reason for this unexpected and unusual behaviour must be sought in the light sensitivity of aquopentacyanoferrite and its susceptibility to thermal decomposition, as pointed out by Iimori.[11] This point has been fully discussed later in this paper. When, however, lamp light is used for the irradiation of ferrocyanide solutions, the after-effect increases with increasing periods of illumination and then attains a practically constant value. The maximum effect is produced after an illumination of 10 minutes. Fig. 2 shows the behaviour in lamp light. In lamp light, as opposed to sunlight, the concentration of aquopentacyanoferrite photochemically formed tends to be kept constant and the light sensitivity of the aquo-salt is negligible under these conditions within the time limit of the exposure (80 mts.).

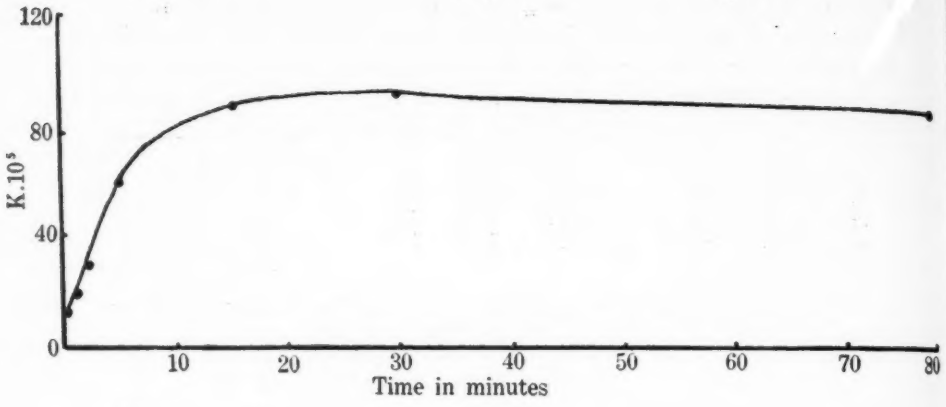

FIG. 2

It was found that the stirring of potassium ferrocyanide solution during pre-illumination did not affect the resulting after-effect rates. It was further observed that air did not exert any influence on these experiments. Solutions of potassium ferrocyanide from which air has been excluded are found to behave exactly like ordinary solutions containing air, so far as the photochemical after-effect is concerned.

DISAPPEARANCE OF ACTIVITY OF PRE-ILLUMINATED FERROCYANIDE

The activity of pre-illuminated potassium ferrocyanide vanishes completely within a short time after darkening. Reactions performed with pre-illuminated potassium ferrocyanide solutions five minutes after darkening give, in the initial stages of the decomposition of hydrogen peroxide, a lower value of the velocity constant than with unilluminated ferrocyanide solution. Experiments also show that there is a measurable interval between the cessation of illumination and the complete disappearance of activity in the pre-illuminated solutions of ferrocyanide. The interval between darkening and mixing of pre-illuminated ferrocyanide with hydrogen peroxide has been indicated by 'T'. The period of pre-insolation was one minute in each case. M/64 aqueous ferrocyanide (10 c.c.) was pre-illuminated by sunlight and then mixed with H_2O_2 in the dark at various time intervals from the moment of darkening. The concentrations of ferrocyanide and hydrogen peroxide in the reaction mixture (50 c.c.) were M/320 and N/6 respectively, as before.

From Tables XX–XXIII it is seen that a measurable after-effect is obtained even in the solution used two minutes after illumination. This diminution of activity of pre-insolated ferrocyanide with time is very sharp in

TABLE XIII

T = 15 *sec.*

t	*a*−*x*	K.10⁵
0	20·20	..
60	19·10	41
120	17·70	48
230	15·60	49
360	13·60	48

TABLE XIV

T = 1 *minute*

t	*a*−*x*	K.10⁵
0	20·35	..
15	20·00	51
83	18·50	50
201	15·95	53
304	14·10	53

TABLE XV

T = 2 *minutes*

t	*a*−*x*	K.10⁵
0	20·50	..
58	18·80	65
150	16·50	63
251	14·20	64

TABLE XVI

T = 5 *minutes*

t	*a*−*x*	K.10⁵
0	20·40	..
60	17·80	99
120	15·90	90
207	13·30	90

TABLE XVII

T = 15 *minutes*

t	*a*−*x*	K.10⁵
0	20·15	..
60	17·00	123
139	13·70	121
180	12·20	121
270	10·05	112

TABLE XVIII

T = 30 *minutes*

t	*a*−*x*	K.10⁵
0	20·40	..
60	17·00	132
123	14·35	124
182	12·45	118

TABLE XIX

T = 80 *minutes*

t	*a*−*x*	K.10⁵
0	20·30	..
78	16·30	122
158	13·35	115
218	11·65	111

TABLE XX

T = ½ *minute*

t	*a*−*x*	K.10⁵
0	20·80	..
15	19·30	217
30	17·70	234
63	14·80	235
105	11·80	235
197	7·50	225

TABLE XXI

T = 1 *minute*

t	*a*−*x*	K.10⁵
0	21·00	..
18	19·90	129
41	18·60	129
133	14·45	122
258	10·70	114
418	8·00	1·3

TABLE XXII

T = 2 *minutes*

t	*a*−*x*	K.10⁵
0	20·90	..
15	20·35	77
30	20·00	64
60	19·10	65
149	16·00	78
276	12·00	87

TABLE XXIII

T = 5 *minutes*

t	*a*−*x*	K.10⁵
0	21·10	..
35	20·60	30
67	20·20	28
120	19·15	35
198	17·30	44
385	12·85	56

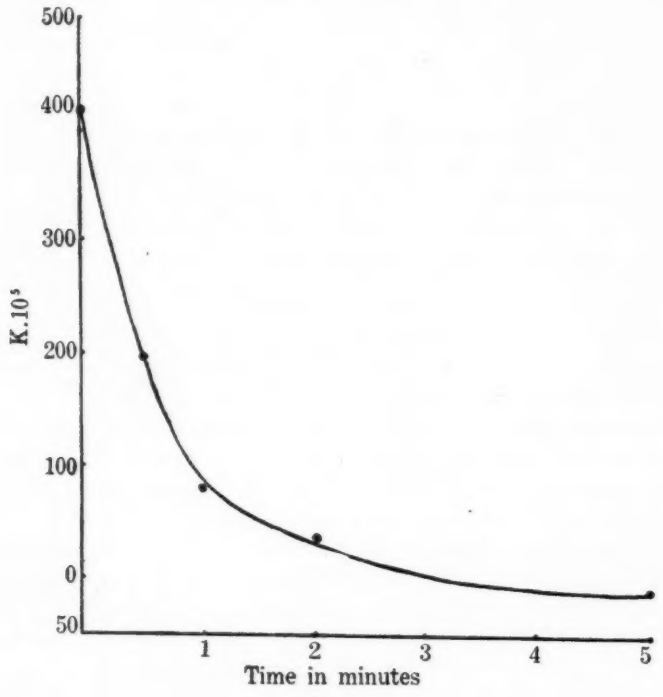

FIG. 3

the beginning and is comparatively slower afterwards. This observation has been graphically illustrated in Fig. 3. It is noticed that a long time interval (5 minutes) between pre-illumination of potassium ferrocyanide and its addition to hydrogen peroxide in the dark results not only in the total

disappearance of the after-effect, but in a distinctly lower rate of decomposition than in experiments with freshly prepared, unilluminated solutions.

Discussion

The results described here substantiate the view originally put forward[1, 3] that the illumination of aqueous ferrocyanide results in the setting up of a photostationary state. The dark equilibrium is shifted far to the right, with increased concentration of potassium aquopentacyanoferrite and hence marked activity of the insolated solution:—

$$K_4Fe(CN)_6 + H_2O \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftharpoons}} K_3Fe(CN)_5H_2O + KCN \qquad (A)$$

The reversion of (A) in the dark takes a measurable time, thus accounting for the results recorded in Tables XX–XXIII.

It has already been suggested that when hydrogen peroxide is added to (A), it is decomposed into water and oxygen, and potassium aquopentacyanoferrite is oxidised to potassium aquopentacyanoferrate as follows:—

$$2\,K_3Fe(CN)_5\,H_2O + H_2O_2 \rightarrow 2\,K_2Fe\,(CN)_5H_2O + 2\,KOH + \text{Energy}$$

It is difficult to formulate the mechanism of the decomposition of hydrogen peroxide. In spite of a large amount of work done on the subject, the exact mechanism of the unimolecular decomposition of hydrogen peroxide is not yet clearly understood. In the experiments of Bredig and co-workers[5] it was suggested by Harber that the decomposition is brought about by the alternate oxidation and reduction of platinum in accordance with the scheme:—

$$yH_2O_2 + x\text{Pt} \rightarrow \text{Pt}_xO_y + yH_2O$$

$$\text{Pt}_xO_y + yH_2O_2 \rightarrow x\text{Pt} + yH_2O + yO_2$$

Wieland,[6] however, assumes two phases in the decomposition of hydrogen peroxide by platinum black, the dehydrogenation of the first molecule, which is actually observed, and the immeasurably rapid reductive fission of the second molecule:—

$$HO\cdot OH \rightarrow O:O + 2H$$

$$HO\cdot OH + 2H \rightarrow 2H_2O$$

Hydrogen peroxide thus behaves as a hydrogenating agent by loss of hydrogen and liberation of molecular oxygen, as a dehydrogenating agent by reacting with hydrogen, and in many reactions as a true oxidising agent.

Haber and Weiss[7] put forward the following mechanism for the decomposition of hydrogen peroxide by a ferrous salt in neutral solution:—

$$Fe^{\cdot\cdot} + H_2O_2 \rightarrow Fe^{\cdot\cdot\cdot}(OH) + OH \quad (1)$$

$$OH + H_2O_2 \rightarrow H_2O + O_2H \quad (2)$$

$$O_2H + H_2O_2 \rightarrow O_2 + H_2O + OH \quad (3)$$

$$Fe^{\cdot\cdot} + OH \rightarrow Fe^{\cdot\cdot\cdot}(OH) \quad (4)$$

The symbol $Fe^{\cdot\cdot\cdot}(OH)$ stands for some unionised compound like $OH \cdot FeSO_4$. The reaction is thus suggested to consist of a chain mechanism, which is carried on by free radicals.

Any decision about the real course of the unimolecular decomposition of hydrogen peroxide must await the results of further research. At this stage a tentative suggestion is put forward which seeks to explain the experimental results obtained in the present investigation. The primary oxidation process involving the formation of aquopentacyanoferrate (III) is a highly exothermic reaction. This primary impulse may bring about the decomposition of a large number of hydrogen peroxide molecules by some yet unelucidated mechanism.

The aquopentacyanoferrate (III) is again reduced to aquopentacyanoferrite (II) as follows:—

$$K_2Fe(CN)_5H_2O + K_4Fe(CN)_6 \rightarrow K_3Fe(CN)_5H_2O + K_3Fe(CN)_6$$

It is well known that potassium ferricyanide is a strong oxidising agent, specially in alkaline solution[8, 9, 10] and will oxidise aquopentacyanoferrite. The above reaction is then written as follows:—

$$K_2Fe(CN)_5H_2O + K_4Fe(CN)_6 \rightleftharpoons K_3Fe(CN)_5H_2O + K_3Fe(CN)_6$$

Thus the stationary concentration of potassium aquopentacyanoferrite tends to be kept constant in presence of a large excess of potassium ferrocyanide. The catalytic system $Fe(CN)_5H_2O^{\cdot\cdot\cdot} \rightleftharpoons Fe(CN)_5H_2O^{\cdot\cdot}$ decomposes hydrogen peroxide at a high velocity thus accounting for the marked photochemical after-effect. In aqueous solution, aquopentacyanoferrite itself undergoes a slow and complicated change on standing in the dark, finally producing ferrocyanide, ferricyanide and ferric hydroxide

$$Fe(CN)_5H_2O^{\cdot\cdot\cdot} \rightarrow Fe(CN)_5^{\cdot\cdot\cdot} + H_2O \quad (B)$$

This decomposition is accelerated by heat and also by light since aquopentacyanoferrite is light sensitive.[11, 12]

Experimental evidence has been adduced for these reactions. The formation of aquopentacyanoferrite on insolation of potassium ferrocyanide solution is shown by testing the solution with *p*-nitrosodimethylaniline, which gives an emerald green colour when added to pre-illuminated solution at once after darkening, or when it is added to potassium ferrocyanide and the mixture insolated. The formation of aquopentacyanoferrite is also shown more spectacularly by aqueous nitrosobenzene when an intense purple colour appears in insolated ferrocyanide solution. These tests are due to Gallenkamp (1916)[13] and Baudisch and Bass[14] (1922) respectively. That the reaction is reversible in the dark is shown by the rapidly diminishing activity of the pre-insolated solution of ferrocyanide in the dark as measured by the rate of hydrogen peroxide decomposition. It is also shown by the fact that a pre-illuminated ferrocyanide solution gives characteristic green and purple colours with *p*-nitrosodimethylaniline and nitrosobenzene only within the first few minutes from the instant of darkening. Williams has also demonstrated the photo-formation of aquopentacyanoferrite from ferrocyanide.[15]

The formation of aquopentacyanoferrate (III) by the reaction between hydrogen peroxide and sodium aquopentacyanoferrite (II) is shown by the violet colour of the reaction mixtures containing no potassium ferrocyanide. The violet end solutions in these experiments do not give any colour reaction with dilute sulphuric acid,[16] nitrosobenzene or *p*-nitrosodimethylaniline, showing the absence of aquopentacyanoferrite (II). If some potassium ferrocyanide is added to such an end solution, it becomes yellow like aquopentacyanoferrite (II) solution and gives positive tests with the above three reagents for aquopentacyanoferrite. The conversion of the aquo-salt (II) into aquo-salt (III) by alkaline potassium ferricyanide has been seen experimentally to be almost instantaneous and this justifies the assumption of the equilibrium reaction mentioned above.

The reactivity of aquopentacyanoferrite towards hydrogen peroxide is largely reduced if the solution is heated or insolated or if it is allowed to age. This diminution has been traced to the destruction of aquopentacyanoferrite ion in the manner shown in Equation B. That the aquopentacyanoferrite is changed into other substances due to heat, light or age is proved by the fact that such a solution does not give the tests characteristics of this ion.

Experiments performed by using lamp light as the illuminant show that the equilibrium in ferrocyanide solution is apparently established in about ten minutes. For shorter exposures, the separate pre-illumination of ferrocyanide gives higher values of the velocity constants with increasing

periods of irradiation, depending upon the absolute amount of absorption of light energy by the solution. The equilibrium is attained only when the illumination is carried over longer periods. Constant values of the velocity constants are hereafter obtained. When the pre-illumination of ferrocyanide is continued for about an hour, the measured magnitude of the photochemical after-effect with such a solution still remains almost constant.

Experiments performed with separately illuminated ferrocyanide solutions added to hydrogen peroxide in the dark just after irradiation, using sunlight as the pre-illuminant, show that the maximum after-effect is obtained with solutions which have been insolated for one minute. Solutions which have been pre-insolated for a longer period give a lower rate of the after-reaction. This behaviour in sunlight, which is different from that observed in lamp light, appears to be due to the more rapid disappearance of aquopentacyanoferrite ions in the former case. The formation of cyanide ions in this process alters the equilibrium conditions due to the suppression of the concentration of aquopentacyanoferrite. The equilibrium point thus gradually shifts to the left as the pre-illumination of aqueous ferrocyanide is prolonged, with the result that the equilibrium concentration of aquopentacyanoferrite is decreased and consequently the after-effect is reduced.

SUMMARY

The photochemical after-effect increases with increasing period of insolation of the ferrocyanide up to a certain stage, and then decreases with further irradiation. This effect is more pronounced with dilute solutions (M/320) than with concentrated solutions (M/64·2). With lamp light as the pre-illuminant, however, the after-effect increases with increasing periods of pre-illumination and finally attains a practically constant value. Stirring of ferrocyanide solution during insolation produces no detectable change in the magnitude of the resulting after-effect. Air has no measurable effect on these experiments. Solutions of ferrocyanide from which air is excluded are found to behave exactly like ordinary solutions containing air, so far as the photochemical after-effect is concerned.

The enhanced reactivity of irradiated ferrocyanide does not disappear completely immediately after darkening, but rapidly diminishes in the dark, although it can be detected in solutions even two minutes after insolation. The photo-formation of potassium aquopentacyanoferrite from ferrocyanide is a reversible reaction. Its reversion to the dark equilibrium takes a measurable time.

The diminution in the reactivity of the aquo-salt (II) due to heat, light and age is traceable to its destruction with the formation of less reactive substances.

The decomposition of hydrogen peroxide is discussed and a mechanism of the photochemical after-effect is proposed involving the alteranate oxidation and reduction of the aquo-salt (II), $Fe(CN)_5H_2O''' \rightleftharpoons Fe(CN)_5H_2O'''$.

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NAPHTHOQUINONE SERIES

Part IV. Reaction of 2: 3-Dichloro-1: 4-naphthoquinone with Ethyl Acetoacetate in Presence of Sodium Ethoxide

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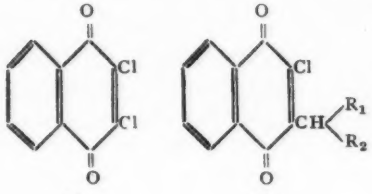
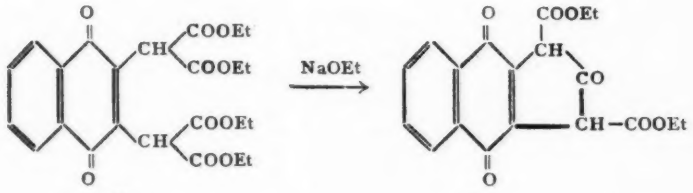
The condensation of 2: 3-dichloro-1: 4-naphthoquinone (I) with compounds containing a reactive methylene group in the presence of sodium ethoxide gives 3-chloro-2-substituted 1: 4-naphthoquinones[1-4] of the type A. In the case of diethyl malonate, in addition to the mono-condensation product,[1] (II) is also formed when excess of diethyl malonate is used.[3] A similar *bis*-condensation product is also formed by the reaction of (I) with excess of ethyl cyanoacetate.[2] These naphthoquinone derivatives are yellow-



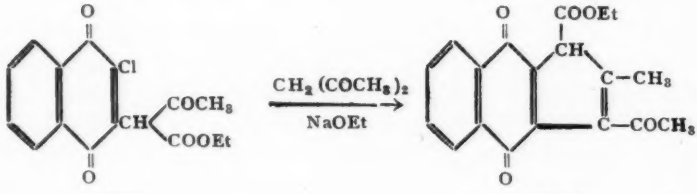
(I) (A)

$R_1 = COCH_3$, COOEt, COPh, CN or $COCO_2Et$

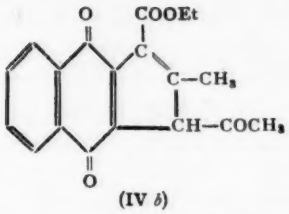
$R_2 = COOEt$, $COCH_3$



(II) (V)



(III) (IV *a*)

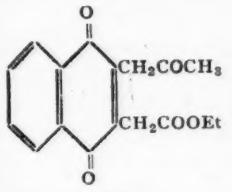


(IV *b*)

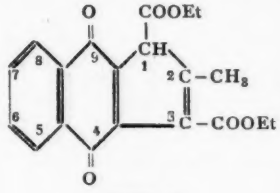
orange in colour. Reaction of ethyl acetoacetate with (I) in the presence of sodium ethoxide gives the yellow-coloured ethyl 3-chloro-1 : 4-naphthoquinone-2-acetoacetate (III) and a chlorine-free garnet-red by-product[4] (B) the constitution of which is now discussed. Condensation of (III) with sodium acetyl acetone gives a garnet-red compound which is constituted as the indene derivative (IV *a*) or (IV *b*).[4] Similarly the ring closure of (II) gives the green-coloured benzindanone derivative[3] (V). The open chain naphthoquinone derivatives (*e.g.*, A and II) are thus yellow-orange in colour, whereas the naphthindene and benzindanone derivatives (IV and V) are garnet-red and green respectively. The reaction of (I) with compounds containing a reactive methylene group and with other compounds has been recently summarized.[5]

Michel[4] and Liebermann[3] have constituted the product (B) referred to above, as (VI) on the basis of its elementary composition and molecular weight (301), determined[4] by the ebullioscopic method using benzene as the solvent. However, a compound constituted as (VI), is more likely to be yellow to orange in colour rather than red.

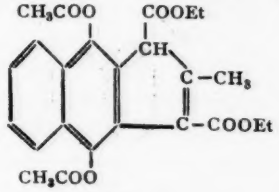
In view of the fact that the deeply coloured compounds (IV) and (V) are formed under similar conditions, it is now suggested that (B) has the constitution, 2-methyl-1 : 3-dicarboethoxy(1-β)-naphthindene-4 : 9-quinone (VII) (*cf.* numbering of 1-β-naphthindene given in the Ring Index[6]). The observation by Hooker,[7] that α : β-unsaturation in the side chain of 1 : 4-naphthoquinone derivatives is associated with deep orange or red colour, also supports the structure (VII) suggested for (B). The latter has closely similar elementary composition as (VI), whereas its molecular weight (354)



(VI)



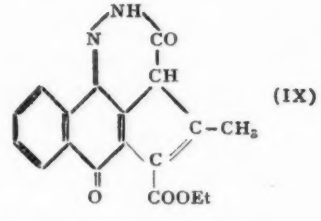
(VII) B



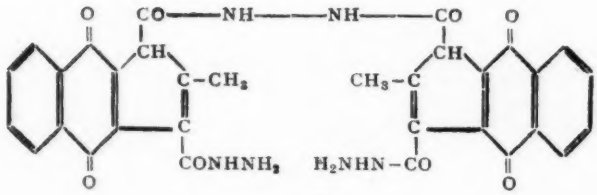
(VIII)

is greater than that of (VI) by 54. Attempts to determine the molecular weight of (B) by Rast's camphor method were unsuccessful because of its deep colour. It was therefore converted into its colourless diacetyl derivative by reductive acetylation. Molecular weight of the latter compound was then readily determined by the Rast's camphor method and it corresponds to the expected value for 4 : 9-diacetoxy-1 : 3-dicarboethoxy-2-methyl-(1-β)-naphthindene (VIII). Since the ebullioscopic method of molecular weight determination is liable to give erroneous results, on account of the small elevation in boiling point of the solvent (*cf.* Pregl),[8] the evidence recorded by Michel as regards the structure of (B) cannot be regarded as conclusive. The molecular weight of the acetyl derivative of (B), on the other hand, could be determined accurately.

Additional evidence in support of the constitution (VII) was provided by the synthesis of (B) from (III) and acetoacetic ester, and the reaction of (B) with hydrazine. When (B) was reacted with aqueous 50% hydrazine hydrate, a cyclic monohydrazine derivative was obtained. The latter may be represented by two alternative structures, but in view of the sluggish reactivity of α : β-unsaturated acid esters, the hydrazine derivative is preferably constituted as (IX). Reaction of (B) with excess of 80% aqueous solution of hydrazine hydrate in boiling alcohol gave a crystalline derivative whose elementary analysis indicates that it is a *bis*-hydrazine derivative which may be represented by a structure, such as (X). The synthesis of (IX) and (X) from (B) further proves the presence of two carboethoxy groups in (B) as shown in the constitution (VII).



(IX)



(X)

Experimental

2-Methyl-1 : 3-dicarboethoxy-(1-β)-naphthindene-4 : 9-quinone (VII)

2 : 3-Dichloro-1 : 4-naphthoquinone (I) (9·87 g.; 0·04 mols.) was added to a boiling solution of ethyl acetoacetate (7·8 g., 0·06 mols.) in absolute alcohol (150 c.c.) in which sodium (1·38 g., 0·06 mols.) was previously dissolved. The solution immediately turned blue and then quickly changed to brownish violet. After refluxing for 2½ hours on a water-bath, the mixture was cooled overnight and the red crystalline substance (sodium salt of VII) was collected (5·8 g.). Crystallization of the latter twice from glacial acetic acid and thrice from alcohol gave garnet-red needles, m.p. 152–3° of (VII) (Found: C, 67·6; H, 5·0. $C_{20}H_{18}O_6$ requires C, 67·8; H, 5·1%). The product is insoluble in aqueous alkali. On boiling with alcoholic alkali and hydrosulphite, it gives a brownish yellow vat.

The alcoholic mother-liquor on concentration (40–50 c.c.) gave yellow crystals of ethyl 2-chloro-1 : 4-naphthoquinone-3-acetoacetate (III) (8·6 g.). The latter after two recrystallizations from alcohol (total 110 c.c.), gave yellow rhombic crystals (5·0 g.), m.p. 106–7° (Found: C, 59·9; H, 4·3. Calc. for $C_{16}H_{13}ClO_5$: C, 59·9; H, 4·1%).

Preparation of (VII) from (III)

Compound (III) (1·0 g.) was added to a boiling solution of ethyl acetoacetate (0·65 g.) in absolute alcohol (35 c.c.) in which sodium (0·115 g.) was previously dissolved. The solution turned blue and then gradually changed to dark brown. The mixture was refluxed on water-bath for 1 hour and cooled to 0°. The brownish red residue (sodium salt of VII) (0·77 g.) was collected and crystallized from glacial acetic acid when it gave garnet-red needles, m.p. 152–6°; undepressed when mixed with (VII).

4 : 9-Diacetoxy-1 : 3-dicarboethoxy-2-methyl-(1-β)-naphthindene (VIII)

A mixture of (VII) (0·5 g.), zinc dust (0·5 g.), fused sodium acetate (0·1 g.) and acetic anhydride (3 c.c.) was gently heated to boil under reflux till the red colour was just discharged (about 5-6 minutes). The mixture was then extracted thrice with 10 c.c. of boiling acetic acid. The acetic acid solution was extracted with ether (250 c.c.). The ether-extract was washed several times with water till it was free from acid. The ether-extract was dried and evaporated, when (VIII) (0·45 g.) was obtained as a colourless residue, m.p. 148–50°. After four crystallizations from benzene-*n*-hexane, it gave colourless needles, m.p. 152–3° (Found: C, 65·8; H, 5·7. $C_{24}H_{24}O_8$ requires

C, 65·5; H, 5·5%). Molecular weight (Rast's Camphor method): 423 and 442. Mean value 433. Molecular weight of $C_{24}H_{24}O_8$: 440.

Synthesis of (IX)

Compound (VII) (1·0 g.) was gradually added to a boiling aqueous solution of hydrazine hydrate (50% w/w; 20 g.). The mixture was heated under reflux for 4–5 hours on a water-bath. The compound dissolved gradually to give a red solution and a yellow compound separated out on further heating. The latter (0·65 g.) was collected, washed with water and alcohol and crystallized from pyridine when it gave yellow flat needles, m.p. 286–9° (decom.) (Found: C, 67·6; H, 4·3; N, 8·6. $C_{18}H_{14}N_2O_4$ requires C, 67·1; H, 4·3; N, 8·7%). The product is sparingly soluble in benzene, alcohol and acetone.

Synthesis of (X)

A boiling solution of hydrazine hydrate (85% w/w; 4 c.c.) in aldehyde-free absolute ethyl alcohol (50 c.c.) was added to a boiling solution of an analytically pure sample of (VII) (1·0 g.) in aldehyde-free ethyl alcohol (100 c.c.). The mixture was vigorously boiled under reflux. After 2 hours brown crystals started separating out. After boiling for 12 hours, the mixture was filtered hot and the brownish yellow prisms collected (0·3 g.), washed with excess of boiling ethyl alcohol and dried. The product does not melt up to 300° (Found: C, 62·3; H. 4·8; N, 13·8. $C_{32}H_{24}N_6O_8$ requires C, 61·9; H, 3·9; N, 13·6%).

SUMMARY

The constitution of the garnet-red compound (B) obtained by the reaction of 2: 3-dichloro-1: 4-naphthoquinone with ethyl acetoacetate in the presence of sodium ethoxide has been reinvestigated. The constitution (VI) assigned by Michel to (B) is not in accord with its colour. The compound is now considered to be 2-methyl-1: 3-dicarboethoxy-(1-β)-naphthindene-4: 9-quinone (VII). The colour of (B), the molecular weight of its diacetoxy derivative (VIII), the synthesis of (B) from ethyl 3-chloro-1: 4-naphthoquinone-2-acetoacetate (III) and the formation of the mono- and *bis*-hydrazine derivatives (IX and X) confirm the new structure, suggested for (B).

We are deeply indebted to the Ministry of Education, Government of India, for award of a Fellowship to one of us (B. S.) and to Dr. T. S. Gore for the microanalyses recorded in the paper.

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